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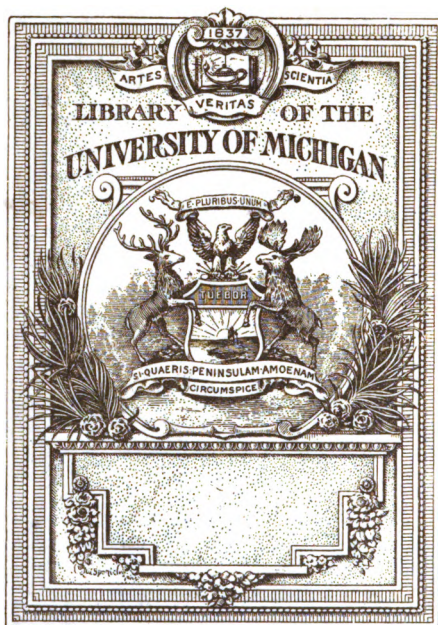
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Alembic Club Reprints—No. 12

THE  
LIQUEFACTION OF GASES

PAPERS

BY

MICHAEL FARADAY, F.R.S.  
(1823-1845)

WITH AN APPENDIX

CONSISTING OF

PAPERS BY THOMAS NORTHMORE  
ON THE COMPRESSION OF GASES  
(1805-1806)

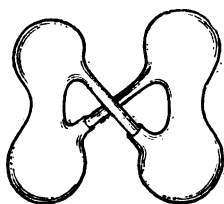
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## PREFACE.



THE papers by Faraday on the Liquefaction of Gases, here reprinted, give an account of the earliest work carried out at the Royal Institution on that most interesting and important subject, with which the Institution has been more or less intimately associated for three-quarters of a century. The extreme beauty and simplicity of Faraday's experiments, as well as the peculiarly felicitous manner in which his various experiments are described, render these papers especially instructive, and suitable for reproduction in the series to which this little volume belongs.

It was considered advisable to reprint Faraday's Historical Statement respecting the Liquefaction of Gases, and, for the sake of greater completeness, to include, in the form of an Appendix, the papers of Mr Northmore which are particularly referred to in that Statement.

L. D.

290653





## I. ON FLUID CHLORINE.\*

*Read March 13, 1823.*

IT is well known that before the year 1810, the solid substance obtained by exposing chlorine, as usually procured, to a low temperature, was considered as the gas itself reduced into that form; and that Sir HUMPHRY DAVY first showed it to be a hydrate, the pure dry gas not being condensible even at a temperature of  $-40^{\circ}$  F.†

I took advantage of the late cold weather to procure crystals of this substance for the purpose of analysis. The results are contained in a short paper in the *Quarterly Journal of Science*, Vol. XV. Its composition is very nearly 27.7 chlorine, 72.3 water, or 1 proportional of chlorine, and 10 of water.

The President of the Royal Society having honoured me by looking at these conclusions, suggested, that an exposure of the substance to heat under pressure, would probably lead to interesting results; the following experiments were commenced at his request. Some hydrate of chlorine was prepared, and being dried as well as could be by pressure in bibulous paper, was introduced into a sealed glass tube, the upper end of which was then hermetically closed. Being placed in water at  $60^{\circ}$ , it underwent no change; but when put into water at  $100^{\circ}$ , the substance fused, the tube became filled with a bright yellow atmosphere, and, on examination, was found to contain two fluid substances: the one, about three-fourths of the whole, was of a faint yellow colour, having very

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\* [From *Philosophical Transactions* for 1823, Vol. 113, pp. 160-165.]

† [See *Alembic Club Reprints*, No. 9, p. 58.]

much the appearance of water ; the remaining fourth was a heavy bright yellow fluid, lying at the bottom of the former, without any apparent tendency to mix with it. As the tube cooled, the yellow atmosphere condensed into more of the yellow fluid, which floated in a film on the pale fluid, looking very like chloride of nitrogen ; and at  $70^{\circ}$  the pale portion congealed, although even at  $32^{\circ}$  the yellow portion did not solidify. Heated up to  $100^{\circ}$  the yellow fluid appeared to boil, and again produced the bright coloured atmosphere.

By putting the hydrate into a bent tube, afterwards hermetically sealed, I found it easy, after decomposing it by a heat of  $100^{\circ}$ , to distil the yellow fluid to one end of the tube, and so separate it from the remaining portion. In this way a more complete decomposition of the hydrate was effected, and, when the whole was allowed to cool, neither of the fluids solidified at temperatures above  $34^{\circ}$ , and the yellow portion not even at  $0^{\circ}$ . When the two were mixed together they gradually combined at temperatures below  $60^{\circ}$ , and formed the same solid substance as that first introduced. If, when the fluids were separated, the tube was cut in the middle, the parts flew asunder as if with an explosion, the whole of the yellow portion disappeared, and there was a powerful atmosphere of chlorine produced ; the pale portion on the contrary remained, and when examined, proved to be a weak solution of chlorine in water, with a little muriatic acid, probably from the impurity of the hydrate used. When that end of the tube in which the yellow fluid lay was broken under a jar of water, there was an immediate production of chlorine gas.

I at first thought that muriatic acid and euchlorine had been formed ; then, that two new hydrates of chlorine had been produced ; but at last I suspected that the chlorine had been entirely separated from the water by the heat,

and condensed into a dry fluid by the mere pressure of its own abundant vapour. If that were true, it followed, that chlorine gas, when compressed, should be condensed into the same fluid, and, as the atmosphere in the tube in which the fluid lay was not very yellow at  $50^{\circ}$  or  $60^{\circ}$ , it seemed probable that the pressure required was not beyond what could readily be obtained by a condensing syringe. A long tube was therefore furnished with a cap and stop-cock, then exhausted of air and filled with chlorine, and being held vertically with the syringe upwards, air was forced in, which thrust the chlorine to the bottom of the tube, and gave a pressure of about 4 atmospheres. Being now cooled, there was an immediate deposit in films, which appeared to be hydrate, formed by water contained in the gas and vessels, but some of the yellow fluid was also produced. As this however might also contain a portion of the water present, a perfectly dry tube and apparatus were taken, and the chlorine left for some time over a bath of sulphuric acid before it was introduced. Upon throwing in air and giving pressure, there was now no solid film formed, but the clear yellow fluid was deposited, and more abundantly still upon cooling. After remaining some time it disappeared, having gradually mixed with the atmosphere above it, but every repetition of the experiment produced the same results.

Presuming that I had now a right to consider the yellow fluid as pure chlorine in the liquid state, I proceeded to examine its properties, as well as I could when obtained by heat from the hydrate. However obtained, it always appears very limpid and fluid, and excessively volatile at common pressure. A portion was cooled in its tube to  $0^{\circ}$ : it remained fluid. The tube was then opened, when a part immediately flew off, leaving the rest so cooled by the evaporation as to remain a fluid

under the atmospheric pressure. The temperature could not have been higher than  $-40^{\circ}$  in this case; as Sir HUMPHRY DAVY has shown that dry chlorine does not condense at that temperature under common pressure. Another tube was opened at a temperature of  $50^{\circ}$ ; a part of the chlorine volatilised, and cooled the tube so much as to condense the atmospheric vapour on it as ice.

A tube having the water at one end and the chlorine at the other was weighed, and then cut in two; the chlorine immediately flew off, and the loss being ascertained was found to be 1.6 grains: the water left was examined and found to contain some chlorine: its weight was ascertained to be 5.4 grains. These proportions, however, must not be considered as indicative of the true composition of hydrate of chlorine; for, from the mildness of the weather during the time when these experiments were made, it was impossible to collect the crystals of hydrate, press, and transfer them, without losing much chlorine; and it is also impossible to separate the chlorine and water in the tube perfectly, or keep them separate, as the atmosphere within will combine with the water, and gradually reform the hydrate.

Before cutting the tube, another tube had been prepared exactly like it in form and size, and a portion of water introduced into it, as near as the eye could judge, of the same bulk as the fluid chlorine: this water was found to weigh 1.2 grains; a result, which, if it may be trusted, would give the specific gravity of fluid chlorine as 1.33; and from its appearance in, and on water, this cannot be far wrong.

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*Note on the Condensation of Muriatic Acid Gas  
into the liquid form. By Sir H. DAVY,  
Bart., Pres. R.S.*

I N desiring Mr. FARADAY to expose the hydrate of chlorine to heat in a closed glass tube, it occurred to me, that one of three things would happen; that it would become fluid as a hydrate; or that a decomposition of water would occur, and euchlorine or muriatic acid be formed; or that the chlorine would separate in a condensed state. This last result having been obtained, it evidently led to other researches of the same kind. I shall hope, on a future occasion, to detail some general views on the subject of these researches. I shall now merely mention, that by sealing the muriate of ammonia and sulphuric acid in a strong glass tube, and causing them to act upon each other, I have procured liquid muriatic acid: and by substituting carbonate for muriate of ammonia, I have no doubt that carbonic acid may be obtained, though in the only trial I have made the tube burst. I have requested Mr. FARADAY to pursue these experiments, and to extend them to all the gases which are of considerable density, or to any extent soluble in water; and I hope soon to be able to lay an account of his results, with some applications of them that I propose to make, before the Society.

I cannot conclude this note without observing, that the generation of elastic substances in close vessels, either with or without heat, offers much more powerful means of approximating their molecules than those dependent upon the application of cold, whether natural or artificial: for, as gases diminish only about  $\frac{1}{480}$  in volume for every — degree of FAHRENHEIT'S scale, beginning at ordinary temperatures, a very slight condensation only

can be produced by the most powerful freezing mixtures, not half as much as would result from the application of a strong flame to one part of a glass tube, the other part being of ordinary temperature: and when attempts are made to condense gases into fluids by sudden mechanical compression, the heat, instantly generated, presents a formidable obstacle to the success of the experiment; whereas, in the compression resulting from their slow generation in close vessels, if the process be conducted with common precautions, there is no source of difficulty or danger; and it may be easily assisted by artificial cold in cases when gases approach near to that point of compression and temperature at which they become vapours.

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## II. ON THE CONDENSATION OF SEVERAL GASES INTO LIQUIDS.\*

*Read April 10, 1823.*

I HAD the honour, a few weeks since, of submitting to the Royal Society a paper on the reduction of chlorine to the liquid state. An important note was added to the paper by the President, on the general application of the means used in this case to the reduction of other gaseous bodies to the liquid state; and in illustration of the process, the production of liquid muriatic acid was described. Sir HUMPHRY DAVY did me the honour to request I would continue the experiments, which I have done under his general direction, and the following are some of the results already obtained:

### *Sulphurous Acid.*

Mercury and concentrated sulphuric acid were sealed

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\* [From Philosophical Transactions for 1823, Vol. 113, pp. 189-198.]

up in a bent tube, and, being brought to one end, heat was carefully applied, whilst the other end was preserved cool by wet bibulous paper. Sulphurous acid gas was produced where the heat acted, and was condensed by the sulphuric acid above; but, when the latter had become saturated, the sulphurous acid passed to the cold end of the tube, and was condensed into a liquid. When the whole tube was cold, if the sulphurous acid were returned on to the mixture of sulphuric acid and sulphate of mercury, a portion was re-absorbed, but the rest remained on it without mixing.

Liquid sulphurous acid is very limpid and colourless, and highly fluid. Its refractive power, obtained by comparing it in water and other media, with water contained in a similar tube, appeared to be nearly equal to that of water. It does not solidify or become adhesive at a temperature of  $0^{\circ}$  F. When a tube containing it was opened, the contents did not rush out as with explosion, but a portion of the liquid evaporated rapidly, cooling another portion so much as to leave it in the fluid state at common barometric pressure. It was however rapidly dissipated, not producing visible fumes, but producing the odour of pure sulphurous acid, and leaving the tube quite dry. A portion of the vapour of the fluid received over a mercurial bath, and examined, proved to be sulphurous acid gas. A piece of ice dropped into the fluid instantly made it boil, from the heat communicated by it.

To prove in an unexceptionable manner that the fluid was pure sulphurous acid, some sulphurous acid gas was carefully prepared over mercury, and a long tube perfectly dry, and closed at one end, being exhausted, was filled with it; more sulphurous acid was then thrown in by a condensing syringe, till there were three or four atmospheres; the tube remained perfectly clear and dry, but on cooling one end to  $0^{\circ}$ , the fluid sulphurous acid con-

densed, and in all its characters was like that prepared by the former process.

A small gage was attached to a tube in which sulphurous acid was afterwards formed, and at a temperature of 45° F. the pressure within the tube was equal to three atmospheres, there being a portion of liquid sulphurous acid present: but as the common air had not been excluded when the tube was sealed, nearly one atmosphere must be due to its presence, so that sulphurous acid vapour exerts a pressure of about two atmospheres at 45° F. Its specific gravity was nearly 1.42.\*

### *Sulphuretted hydrogen.*

A tube being bent, and sealed at the shorter end, strong muriatic acid was poured in through a small funnel, so as nearly to fill the short leg without soiling the long one. A piece of platinum foil was then crumpled up and pushed in, and upon that were put fragments of

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\* I am indebted to Mr. DAVIES GILBERT, who examined with much attention the results of these experiments, for the suggestion of the means adopted to obtain the specific gravity of some of these fluids. A number of small glass bulbs were blown and hermetically sealed; they were then thrown into alcohol, water, sulphuric acid, or mixtures of these, and when any one was found of the same specific gravity as the fluid in which it was immersed, the specific gravity of the fluid was taken: thus a number of hydrometrical bulbs were obtained; these were introduced into the tubes in which the substances were to be liberated; and ultimately, the dry liquids obtained, in contact with them. It was then observed whether they floated or not, and a second set of experiments were made with bulbs lighter or heavier as required, until a near approximation was obtained. Many of the tubes burst in the experiments, and in others difficulties occurred from the accidental fouling of the bulb by the contents of the tube. One source of error may be mentioned in addition to those which are obvious, namely, the alteration of the bulk of the bulb by its submission to the pressure required to keep the substance in the fluid state.



sulphuret of iron, until the tube was nearly full. In this way action was prevented until the tube was sealed. If it once commences, it is almost impossible to close the tube in a manner sufficiently strong, because of the pressing out of the gas. When closed, the muriatic acid was made to run on to the sulphuret of iron, and then left for a day or two. At the end of that time, much proto-muriate of iron had formed, and on placing the clean end of the tube in a mixture of ice and salt, warming the other end if necessary by a little water, sulphuretted hydrogen in the liquid state distilled over.

The liquid sulphuretted hydrogen was colourless, limpid, and excessively fluid. Ether, when compared with it in similar tubes, appeared tenacious and oily. It did not mix with the rest of the fluid in the tube, which was no doubt saturated, but remained standing on it. When a tube containing it was opened, the liquid immediately rushed into vapour; and this being done under water, and the vapour collected and examined, it proved to be sulphuretted hydrogen gas. As the temperature of a tube containing some of it rose from  $0^{\circ}$  to  $45^{\circ}$ , part of the fluid rose in vapour, and its bulk diminished; but there was no other change: it did not seem more adhesive at  $0^{\circ}$  than at  $45^{\circ}$ . Its refractive power appeared to be rather greater than that of water; it decidedly surpassed that of sulphurous acid. A small gage being introduced into a tube in which liquid sulphuretted hydrogen was afterwards produced, it was found that the pressure of its vapour was nearly equal to 17 atmospheres at the temperature of  $50^{\circ}$ .

The gages used were made by drawing out some tubes at the blow-pipe table until they were capillary, and of a trumpet form; they were graduated by bringing a small portion of mercury successively into their different parts; they were then sealed at the fine end, and a portion of

mercury placed in the broad end ; and in this state they were placed in the tubes, so that none of the substances used, or produced, could get to the mercury, or pass by it to the inside of the gage. In estimating the number of atmospheres, one has always been subtracted for the air left in the tube.

The specific gravity of sulphuretted hydrogen appeared to be 0.9.

### *Carbonic acid.*

The materials used in the production of carbonic acid, were carbonate of ammonia and concentrated sulphuric acid ; the manipulation was like that described for sulphuretted hydrogen. Much stronger tubes are however required for carbonic acid than for any of the former substances, and there is none which has produced so many or more powerful explosions. Tubes which have held fluid carbonic acid well for two or three weeks together, have, upon some increase in the warmth of the weather, spontaneously exploded with great violence ; and the precautions of glass masks, goggles, &c. which are at all times necessary in pursuing these experiments, are particularly so with carbonic acid.

Carbonic acid is a limpid colourless body, extremely fluid, and floating upon the other contents of the tube. It distils readily and rapidly at the difference of temperature between  $32^{\circ}$  and  $0^{\circ}$ . Its refractive power is much less than that of water. No diminution of temperature to which I have been able to submit it, has altered its appearance. In endeavouring to open the tubes at one end, they have uniformly burst into fragments, with powerful explosions. By inclosing a gage in a tube in which fluid carbonic acid was afterwards produced, it was found that its vapour exerted a pressure of 36 atmospheres at a temperature of  $32^{\circ}$ .

It may be questioned, perhaps, whether this and other similar fluids obtained from materials containing water, do not contain a portion of that fluid ; in as much as its absence has not been proved, as it may be with chlorine, sulphurous acid, cyanogen, and ammonia. But besides the analogy which exists between the latter and the former, it may also be observed in favour of their dryness, that any diminution of temperature causes the deposition of a fluid from the atmosphere, precisely like that previously obtained ; and there is no reason for supposing that these various atmospheres, remaining as they do in contact with concentrated sulphuric acid, are not as dry as atmospheres of the same kind would be over sulphuric acid at common pressure.

*Euchlorine.*

Fluid euchlorine was obtained by inclosing chlorate of potash and sulphuric acid in a tube, and leaving them to act on each other for 24 hours. In that time there had been much action, the mixture was of a dark reddish brown, and the atmosphere of a bright yellow colour. The mixture was then heated up to  $100^{\circ}$ , and the unoccupied end of the tube cooled to  $0^{\circ}$  ; by degrees the mixture lost its dark colour, and a very fluid ethereal looking substance condensed. It was not miscible with a small portion of the sulphuric acid which lay beneath it ; but when returned on to the mass of salt and acid, it was gradually absorbed, rendering the mixture of a much deeper colour even than itself.

Euchlorine thus obtained is a very fluid transparent substance, of a deep yellow colour. A tube containing a portion of it in the clean end, was opened at the opposite extremity ; there was a rush of euchlorine vapour, but the salt plugged up the aperture : whilst clearing this

away, the whole tube burst with a violent explosion, except the small end in a cloth in my hand, where the euchlorine previously lay, but the fluid had all disappeared.

*Nitrous oxide.*

Some nitrate of ammonia, previously made as dry as could be by partial decomposition, by heat in the air, was sealed up in a bent tube, and then heated in one end, the other being preserved cool. By repeating the distillation once or twice in this way, it was found, on after-examination, that very little of the salt remained undecomposed. The process requires care, I have had many explosions occur with very strong tubes, and at considerable risk.

When the tube is cooled, it is found to contain two fluids, and a very compressed atmosphere. The heavier fluid on examination proved to be water, with a little acid and nitrous oxide in solution; the other was nitrous oxide. It appears in a very liquid, limpid, colourless state; and so volatile that the warmth of the hand generally makes it disappear in vapour. The application of ice and salt condenses abundance of it into the liquid state again. It boils readily by the difference of temperature between  $50^{\circ}$  and  $0^{\circ}$ . It does not appear to have any tendency to solidify at  $-10^{\circ}$ . Its refractive power is very much less than that of water, and less than any fluid that has yet been obtained in these experiments, or than any known fluid. A tube being opened in the air, the nitrous oxide immediately burst into vapour. Another tube opened under water, and the vapour collected and examined, it proved to be nitrous oxide gas. A gage being introduced into a tube, in which liquid nitrous oxide was afterwards produced, gave the pressure of its vapour as equal to above 50 atmospheres at  $45^{\circ}$ .

*Cyanogen.*

Some pure cyanuret of mercury was heated until perfectly dry. A portion was then inclosed in a green glass tube, in the same manner as in former instances, and being collected to one end, was decomposed by heat, whilst the other end was cooled. The cyanogen soon appeared as a liquid: it was limpid, colourless, and very fluid; not altering its state at the temperature of  $0^{\circ}$ . Its refractive power is rather less, perhaps, than that of water. A tube containing it being opened in the air, the expansion within did not appear to be very great; and the liquid passed with comparative slowness into the state of vapour, producing great cold. The vapour, being collected over mercury, proved to be pure cyanogen.

A tube was sealed up with cyanuret of mercury at one end, and a drop of water at the other; the fluid cyanogen was then produced in contact with the water. It did not mix, at least in any considerable quantity, with that fluid, but floated on it, being lighter, though apparently not so much so as ether would be. In the course of some days, action had taken place, the water had become black, and changes, probably such as are known to take place in an aqueous solution of cyanogen, occurred. The pressure of the vapour of cyanogen appeared by the gage to be 3.6 or 3.7 atmospheres at  $45^{\circ}$  F. Its specific gravity was nearly 0.9.

*Ammonia.*

In searching after liquid ammonia, it became necessary, though difficult, to find some dry source of that substance; and I at last resorted to a compound of it, which I had occasion to notice some years since with chloride of silver.\* When dry chloride of silver is put into ammoniacal gas,

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\* Quarterly Journal of Science, Vol. V. p. 74.

as dry as it can be made, it absorbs a large quantity of it; 100 grains condensing above 130 cubical inches of the gas: but the compound thus formed is decomposed by a temperature of 100° F. or upwards. A portion of this compound was sealed up in a bent tube and heated in one leg, whilst the other was cooled by ice or water. The compound thus heated under pressure fused at a comparatively low temperature, and boiled up, giving off ammoniacal gas, which condensed at the opposite end into a liquid.

Liquid ammonia thus obtained was colourless, transparent, and very fluid. Its refractive power surpassed that of any other of the fluids described, and that also of water itself. From the way in which it was obtained, it was evidently as free from water as ammonia in any state could be. When the chloride of silver is allowed to cool, the ammonia immediately returns to it, combining with it, and producing the original compound. During this action a curious combination of effects takes place: as the chloride absorbs the ammonia, heat is produced, the temperature rising up nearly to 100°; whilst a few inches off, at the opposite end of the tube, considerable cold is produced by the evaporation of the fluid. When the whole is retained at the temperature of 60°, the ammonia boils till it is dissipated and re-combined. The pressure of the vapour of ammonia is equal to about 6.5 atmospheres at 50°. Its specific gravity was 0.76.

#### *Muriatic acid.*

When made from pure muriate of ammonia and sulphuric acid, liquid muriatic acid is obtained colourless, as Sir HUMPHRY DAVY had anticipated. Its refractive power is greater than that of nitrous oxide, but less than that of water; it is nearly equal to that of carbonic acid.

The pressure of its vapour at the temperature of  $50^{\circ}$ , is equal to about 40 atmospheres.

*Chlorine.*

The refractive power of fluid chlorine is rather less than that of water. The pressure of its vapour at  $60^{\circ}$  is nearly equal to 4 atmospheres.

Attempts have been made to obtain hydrogen, oxygen, fluorboracic, fluosilicic, and phosphuretted hydrogen gases in the liquid state; but though all of them have been subjected to great pressure, they have as yet resisted condensation. The difficulty with regard to fluoboric gas consists, probably, in its affinity for sulphuric acid, which, as Dr. DAVY has shown, is so great as to raise the sulphuric acid with it in vapour. The experiments will however be continued on these and other gases, in the hopes that some of them, at least, will ultimately condense.

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### III. HISTORICAL STATEMENT RESPECTING THE LIQUEFACTION OF GASES\*.

I WAS not aware at the time when I first observed the liquefaction of chlorine gas†, nor until very lately, that any of the class of bodies called *gases*, had been reduced into the fluid form; but, having during the last few weeks sought for instances where such results might have been afforded without the knowledge of the experimenter, I was surprised to find several recorded cases. I have thought it right therefore to bring these cases

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\* [From *The Quarterly Journal of Science*, vol. xvi. (January 1824), pp. 229-240.]

† *Phil. Transactions*, 1823, pp. 160, 189.

together, and only justice to endeavour to secure for them a more general attention, than they appear as yet to have gained. I shall notice in chronological order, the fruitless, as well as the successful, attempts, and those which probably occurred without being observed, as well as those which were remarked and described as such.

*Carbonic Acid, &c.*—The *Philosophical Transactions* for 1797, contain, p. 222, an account of experiments made by Count Rumford, to determine the force of fired gunpowder. Dissatisfied both with the deductions drawn, and the means used previously, that philosopher proceeded to fire gunpowder in cylinders of a known diameter and capacity, and closed by a valve loaded with a weight that could be varied at pleasure. By making the vessel strong enough and the weight sufficiently heavy, he succeeded in confining the products within the space previously occupied by the powder. The Count's object induced him to vary the quantity of gunpowder in different experiments, and to estimate the force exerted only at the moment of ignition, when it was at its maximum. This force which he found to be prodigious, he attributes to aqueous vapour intensely heated, and makes no reference to the force of the gaseous bodies evolved. Without considering the phenomena which it is the Count's object to investigate, it may be remarked, that in many of the experiments made by him, some of the gases, and especially carbonic acid gas, were probably reduced to the liquid state. The Count says,

“When the force of the generated elastic vapour was sufficient to raise the weight, the explosion was attended by a very sharp and surprisingly loud report; but when the weight was not raised, as also when it was only a little moved, but not sufficiently to permit the leather stopper to be driven quite out of the bore, and the



elastic fluid to make its escape, the report was scarcely audible at the distance of a few paces, and did not at all resemble the report which commonly attends the explosion of gunpowder. It was more like the noise which attends the breaking of a small glass tube, than any thing else to which it could be compared. In many of the experiments, in which the elastic vapour was confined, this feeble report attending the explosion of the powder, was immediately followed by another noise totally different from it, which appeared to be occasioned by the falling back of the weight upon the end of the barrel, after it had been a little raised, but not sufficiently to permit the leather stopper to be driven quite out of the bore. In some of these experiments a very small part only of the generated elastic fluid made its escape, in these cases the report was of a peculiar kind, and though perfectly audible at some considerable distance, yet not at all resembling the report of a musket. It was rather a very strong sudden hissing, than a clear distinct and sharp report."

In another place it is said, "What was very remarkable in all these experiments, in which the generated elastic vapour was completely confined, was the small degree of expansive force which this vapour appeared to possess, after it had been suffered to remain a few minutes, or even only a few seconds, confined in the barrel; for upon raising the weight, by means of its lever, and suffering this vapour to escape, instead of escaping with a loud report it rushed out with a hissing noise, hardly so loud or so sharp as the report of a common air-gun, and its effects against the leather stopper, by which it assisted in raising the weight, were so very feeble as not to be sensible." This the Count attributes to the formation of a hard mass, like a stone, within the cylinder, occasioned by the condensation of what was, at the moment of igni-

tion, an elastic fluid. Such a substance was always found in these cases ; but when the explosion raised the weight and blew out the stopper, nothing of this kind remained.

The effects here described both of elastic force and its cessation on cooling, may evidently be referred as much to carbonic acid and perhaps other gases as to water. The strong sudden hissing observed as occurring when only a little of the products escaped, may have been due to the passage of the gases into the air, with comparatively but little water, the circumstances being such as were not sufficient to confine the former, though they might the latter ; for it cannot be doubted but that in similar circumstances, the elastic force of carbonic acid would far surpass that of water. Count Rumford says, that the gunpowder made use of, when well shaken together, occupied rather less space than an equal weight of water. The quantity of residuum before referred to, left by a given weight of gunpowder, is not mentioned, so that the actual space occupied by the vapour of water, carbonic acid, &c., at the moment of ignition, cannot be inferred ; there can, however, be but little doubt that when perfectly confined they were in the state of the substances, in M. Cagniard de la Tour's experiments\*.

When allowed to remain a few minutes, or even seconds, the expansive force at first observed, diminished exceedingly, so as scarcely to surpass that of the air in a charged air-gun. Of course all that was due to the vaporization of water and some of the other products would cease, as soon as the mass of metal had absorbed the heat, and they would concrete into the hard substance found in the cylinder : but it does not seem too much to suppose, that so much carbonic acid was generated in the combustion, as would, if confined, on the cooling of the

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\* See vol. xv. p. 145, of this Journal.

apparatus, have been equal to many atmospheres, but that being condensible, a part became liquid, and thus assisted in reducing the force within, to what it was found to be.

*Ammonia.*—I find the condensation of ammoniacal gas referred to in *Thomson's System*, first edition, i. 405, and other editions; *Henry's Chemistry*, i. 237; *Accum's Chemistry*, i. 310; *Murray's Chemistry*, ii. 73; and *Thenard's Traité de Chimie*, ii. 133. Mr. Accum refers to the experiments of Fourcroy and Vauquelin, *Ann. de Chimie*, xxix. 289, but has mistaken their object. Those chemists used highly saturated solution of ammonia, see pp. 281, 286, and not the gas; and their experiments on gases, namely, sulphurous acid gas, muriatic acid gas, and sulphuretted hydrogen gas, they state were fruitless, p. 287. "All we can say is, that the condensation of most of these gases was above three fourths of their volume."

Thomson, Henry, Murray, and, I suppose, Thenard, refer to the experiments of Guyton de Morveau, *Ann. de Chimie*, xxix. 291, 297. Thomson states the result of liquefaction at a temperature of  $-45^{\circ}$ , without referring to the doubt, that Morveau himself raises, respecting the presence of water in the gas; but Murray, Henry, and Thenard, in their statements notice its probable presence. Morveau's experiment was made in the following manner: a glass retort was charged with the usual mixture of muriate of ammonia, and quick lime, the former material being sublimed, and the latter carefully made from white marble, so as to exclude water as much as possible. The beak of the retort was then adapted to an apparatus consisting of two balloons, and two flasks successively connected together, and luted by fat lute. The balloons were empty, the first flask contained mercury, the second, water. Heat was then applied to the retort, and the first globe cooled to  $-21.25^{\circ}\text{C.}$ , aqueous vapours soon rose,

which condensed as water in the neck of the retort, and as ice in the first balloon. Continuing the heat, ammoniacal gas was disengaged, and it escaped by the last flask containing water, without anything being perceived in the second balloon. This balloon was then cooled to  $-43.25^{\circ}\text{C}$ ., and then drops of a fluid lined its interior, and ultimately united at the bottom of the vessel. When the thermometer in the cooling mixture stood at  $-36.25^{\circ}\text{C}$ ., the fluid already deposited preserved its state, but no further portions were added to it; reducing the temperature again to  $-41^{\circ}\text{C}$ ., and hastening the disengagement of ammoniacal gas, the liquid in the second balloon augmented in volume. Very little gas escaped from the last flask, and the pressure inwards was such as to force the oil of the lute into the balloon where it congealed. Finally, the apparatus was left to regain the temperature of the atmosphere, and as it approached to it, the liquid of the second balloon became gaseous. The fluid in the first balloon became liquid, as soon as the temperature had reached  $-21.25^{\circ}\text{C}$ .

M. Morveau remarks on this experiment, that it appears certain that ammoniacal gas made as dry as it can be, by passing into a vessel in which water would be frozen, and reduced to a temperature of  $-21^{\circ}\text{C}$ ., condenses into a liquid at the temperature of  $-48^{\circ}\text{C}$ ., and resumes its elastic form again as the temperature is raised; but he proposes to repeat the experiment and examine whether a portion of the gas so dried, when received over mercury would not yield water to well calcined potash, "for as it is seen that water charged with a little of the gas, remained liquid in the first balloon, at a temperature of  $-21^{\circ}$ , it is possible that a much smaller quantity of water united to a much larger quantity of the gas, would become capable of resisting a temperature of  $-48^{\circ}\text{C}$ ."

Sir H. Davy, who refers to this experiment in his *Elements of Chemical Philosophy*, p. 267, urges the uncertainty attending it, on the same grounds that Morveau himself had done; and now that the strength of the vapour of dry liquid ammonia is known, it cannot be doubted that M. Morveau had obtained in his second balloon only a very concentrated solution of ammonia in water. I find that the strength of the vapour of ammonia dried by potash, is equal to about that of 6.5 atmospheres at 50° F\*. and according to all analogy it would require a very intense degree of cold, and one at present beyond our means, to compensate this power and act as an equivalent to it.

*Sulphurous Acid Gas.*—It is said that sulphurous acid gas has been condensed into a fluid by Monge and Clouet, but I have not been able to find the description of their process. It is referred to by Thomson, in his *System*, first edition, ii. 24, and in subsequent editions; by Henry, in his *Elements*, i. 341; by Accum, in his *Chemistry*, i. 319; by Aikin, *Chemical Dictionary*, ii. 391; by Nicholson, *Chemical Dictionary*, article, gas (Sulphurous acid); and by Murray, in his *System*, ii. 405. All these authors mention the simultaneous application of cold and pressure, but Thomson alone refers to any authority, and that is Fourcroy, ii. 74.

It is curious that Fourcroy does not, however, mention condensation as one of the means employed by Monge and Clouet, but merely says the gas is capable of liquefaction at 28° of cold. "This latter property," he adds, "discovered by citizens Monge and Clouet, and by which it is distinguished from all the other gases, appears to be owing to the water which it holds in solution, and to which it adheres so strongly as to prevent an accurate

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\* *Philosophical Transactions*, 1823, p. 197.

estimate of the proportions of its radical and acidifying principles."

Notwithstanding Fourcroy's objection, there can be but little reason to doubt that Monge and Clouet did actually condense the gas, for I have since found that from the small elastic force of its vapour at common temperatures (being equal to that of about two atmospheres only \*) a comparatively moderate diminution of temperature is sufficient to retain it fluid at common pressure, or a moderate additional pressure to retain it so at common temperature ; so that whether these philosophers applied cold only as Fourcroy mentions, or cold and pressure, as stated by the other chemists, they would succeed in obtaining it in the liquid form.

*Chlorine.*—M. de Morveau, whilst engaged on the application of the means best adapted to destroy putrid effluvia and contagious miasmata, was led to the introduction of chlorine as the one most excellent for this purpose ; and he proposed the use of phials, containing the requisite materials, as sources of the substance. One described in his *Traité des Moyens de désinfecter l'air* (1801), was of the capacity of two cubical inches nearly ; about 62 grains of black oxide of manganese in coarse powder was introduced, and then the bottle two-thirds filled with nitro-muriatic acid ; it was shaken, and in a short time chlorine was abundantly disengaged. M. Morveau remarks upon the facility with which the chlorine is retained in these bottles ; one, thus prepared, and forgotten, when opened at the end of eight years, gave an abundant odour of chlorine.

I had an impression on my mind that M. de Morveau had proposed the use of phials similarly charged, but made strong, well stoppered, and confined by a screw in

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\* *Philosophical Transactions*, 1823, p. 192.

a frame, so that no gas should escape, except when the screw and stopper were loosened ; but I have searched for an account of such phials without being able to find any. If such have been made, it is very probable that in some circumstances, liquid chlorine has existed in them, for as its vapour at 60°F. has only a force of about four atmospheres\*, a charge of materials might be expected frequently to yield much more chlorine than enough to fill the space, and saturate the fluid present ; and the excess would of course take the liquid form. If such vessels have not been made, our present knowledge of the strength of the vapour of chlorine will enable us to construct them of a much more convenient and portable form than has yet been given to them.

*Arseniuretted Hydrogen.*—This is a gas which it is said has been condensed so long since as 1805. The experiment was made by Stromeyer, and was communicated, with many other results relating to the same gas, to the Göttingen Society, Oct. 12, 1805. See *Nicholson's Journal*, xix. 382 ; also, *Thenard Traité de Chimie*, i. 373 ; *Brandé's Manual*, ii. 212 ; and *Annales de Chimie*, lxiv. 303. None of these contain the original experiment ; but the following quotation is from *Nicholson's Journal*. The gas was obtained over the pneumatic apparatus, by digesting an alloy of fifteen parts tin and one part arsenic, in strong muriatic acid. "Though the arsenicated hydrogen gas retains its aëriform state under every known degree of atmospheric temperature and pressure, Professor Stromeyer condensed it so far as to reduce it in part to a liquid, by immersing it in a mixture of snow and muriate of lime, in which several pounds of quicksilver had been frozen in the course of a few minutes." From the circumstance of its being reduced only in part

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\* *Ibid.* p. 198.

to a liquid, we may be led to suspect that it was rather the moisture of the gas that was condensed than the gas itself; a conjecture which is strengthened in my mind from finding that a pressure of three atmospheres was insufficient to liquefy the gas at a temperature of  $0^{\circ}\text{F}$ .

*Chlorine.*—The most remarkable and direct experiments I have yet met with in the course of my search after such as were connected with the condensation of gases into liquids, are a series made by Mr. Northmore, in the years 1805-6. It was expected by this gentleman "that the various affinities which take place among the gases under the common pressure of the atmosphere, would undergo considerable alteration by the influence of condensation;" and it was with this in view that the experiments were made and described. The results of liquefaction were therefore incidental, but at present it is only of them I wish to take notice. Mr. Northmore's papers may be found in *Nicholson's Journal*, xii. 368, xiii. 233. In the first is described his apparatus, namely, a brass condensing pump; pear-shaped glass receivers, containing from three and a half to five cubic inches, and a quarter of an inch thick; and occasionally a syphon gauge. Sometimes as many as eighteen atmospheres were supposed to have been compressed into the vessel, but it is added, that the quantity cannot be depended on, as the tendency to escape even by the side of the piston, rendered its confinement very difficult.

Now that we know the pressure of the vapour of chlorine, there can be no doubt that the following passage describes a true liquefaction of that gas. "Upon the compression of nearly two pints of oxygenated muriatic acid gas in a receiver, two and a quarter cubic inches capacity, it speedily became converted into a yellow *fluid*, of such extreme volatility, under the common pressure of the atmosphere, that it instantly evaporated upon open-



ing the screw of the receiver ; I need not add, that this fluid, so highly concentrated, is of a most insupportable pungency." "There was a trifling residue of a yellowish substance left after the evaporation, which probably arose from a small portion of the oil and grease used in the machine," &c. xiii. 234.

*Muriatic Acid.*—Operating upon muriatic acid, Mr. Northmore obtained such results as induced him to state he could liquefy it in any quantity, but as the pressure of its vapour at 50°F. is equal to about 40 atmospheres\*, he must have been mistaken. The following is his account: "I now proceeded to the muriatic acid gas, and upon the condensation of a small quantity of it, a beautiful green-coloured substance adhered to the side of the receiver, which had all the qualities of muriatic acid ; but upon a large quantity, four pints, being condensed, the result was a yellowish green glutinous substance, which does not evaporate, but is instantly absorbed by a few drops of water ; it is of a highly pungent quality, being the essence of muriatic acid. As this gas easily becomes fluid, there is little or no elasticity, so that any quantity may be condensed without danger. My method of collecting this and other gases, which are absorbable by water, is by means of an exhausted Florence flask, (and in some cases an empty bladder) connected by a stop cock with the extremity of the retort." xiii. 235. It seems probable that the facility of condensation, and even combination, possessed by muriatic acid gas in contact with oil of turpentine, may belong to it under a little pressure, in contact with common oil, and thus have occasioned the results Mr. Northmore describes.

*Sulphurous Acid Gas.*—With regard to this gas, Mr.

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\* *Philosophical Transactions*, 1823, p. 198.

Northmore says, "having collected about a pint and a half of sulphurous acid gas, I proceeded to condense it in the three cubic inch receiver, but after a very few pumps the forcing piston became immoveable, being completely choked by the operation of the gas. A sufficient quantity had, however, been compressed to form vapour, and a thick slimy fluid, of a dark yellow colour, began to trickle down the sides of the receiver, which immediately evaporated with the most suffocating odour upon the removal of the pressure." xiii. 236. This experiment, Mr. Northmore remarks, corroborates the assertion of Monge and Clouet, that by cold and pressure they had condensed this gas. The fluid above described was evidently contaminated with oil, but from its evaporation on removing the pressure, and from the now ascertained low pressure of the vapour of sulphurous acid, there can be no hesitation in admitting that it was sulphurous acid liquefied.

The results obtained by Mr. Northmore, with chlorine gas and sulphurous acid gas, are referred to by Nicholson, in his *Chemical Dictionary*, 8vo. Articles, Gas (muriatic acid oxygenized) and Gas (sulphurous acid); and that of chlorine is referred to by Murray, in his *System*, ii. 550; although at page 405 of the same volume, he says that, only sulphurous acid "and ammonia of these gases that are at natural temperatures permanently elastic, have been found capable of this reduction."

*Carbonic Acid.*—Another experiment in which it is very probable that liquid carbonic acid has been produced, is one made by Mr. Babbage, about the year 1813. The object Mr. Babbage had in view, was to ascertain whether pressure would prevent decomposition, and it was expected that either that would be the case, or that decomposition would go on, and the rock be split by the expansive force of carbonic acid gas. The place was Chudley

rocks, Devonshire, where the limestone is dark and of a compact texture. A hole, about 30 inches deep and two inches in diameter, was made by the workmen in the usual way, it penetrated directly downwards into the rock; a quantity of strong muriatic acid, equal to perhaps a pint and a half, was then poured in, and immediately a conical wooden plug, that had previously been soaked in tallow, was driven hard into the mouth of the hole. The persons about then retired to a distance to watch the result, but nothing apparent happened, and, after waiting some time, they left the place. The plug was not loosened at the time, nor was any further examination of the state of things made: but it is very probable that if the rock were sufficiently compact in that part, the plug tight, and the muriatic acid in sufficient quantity, that a part of the carbonic acid had condensed into a liquid, and thus, though it permitted the decomposition, prevented that development of power which Mr. Babbage expected would have torn the rock asunder.

*Oil Gas Vapour.*—An attempt has been made by Mr Gordon, within the last few years, and is still continued, to introduce condensed gas into use in the construction of portable, elegant, and economical gas lamps. Oil gas has been made use of, and, I believe, as many as thirty atmospheres have been thrown into vessels, which, furnished with a stop cock and jet, have afterwards allowed of its gradual expansion and combustion. During the condensation of the gas in this manner, a liquid has been observed to deposit from it. It is not, however, a result of the liquefaction of the gas, but the deposition of a vapour (using the terms gas and vapour in their common acceptation) from it, and when taken out of the vessel it remains a liquid at common temperatures and pressures; may be purified by distillation, in the ordinary way, and

will even bear a temperature of  $170^{\circ}\text{F}$ . before it boils, at ordinary pressure. It is the substance referred to by Dr Henry, in the *Philosophical Transactions*, 1821, p. 159.

There is no reason for believing that oil gas, or olefiant gas, has, as yet, been condensed into a liquid, or that it will take that form at common temperatures under a pressure of five, or ten, or even twenty atmospheres. If it were possible, a small, safe, and portable gas lamp would immediately offer itself to us, which might be filled with liquid without being subject to any greater force than the strength of its vapour, and would afford an abundant supply of gas as long as any of the liquid remained. Immediately upon the condensation of cyanogen, which takes place at  $50^{\circ}\text{F}$ . at a pressure under four atmospheres, I made such a lamp with it. It succeeded perfectly, but, of course, either the expense of the gas, the faint light of its flame, or its poisonous qualities, would preclude its application. But we may, perhaps, without being considered extravagant, be allowed to search in the products of oil, resins, coal, &c., distilled, or otherwise treated, with this object in view, for a substance, which being a gas at common temperatures and pressure, shall condense into a liquid, by a pressure of from two to six or eight atmospheres, and which being combustible, shall afford a lamp of the kind described\*.

*Atmospheric Air.*—As my object is to draw attention to the results obtained in the liquefaction of gases before the date of those described in the *Philosophical Transactions* for 1823, I need not, perhaps, refer to the notice given in the *Annals of Philosophy*, N.S. vi. 66, of the supposed liquefaction of atmospheric air, by Mr. Perkins, under a pressure of about 1100 atmospheres, but as such

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\* In reference to the probability of such results, see a paper "On Olefiant Gas." *Annals of Philosophy*, N.S. iii. 37.

a result would be highly interesting, and is the only additional one on the subject I am acquainted with, I am desirous of doing so, as well also to point out the remarkable difference between that result and those which are the subject of this and the other papers referred to. Mr. Perkins informed me that the air upon compression disappeared, and in its place was a small quantity of a fluid, which remained so when the pressure was removed, which had little or no taste, and which did not act on the skin. As far as I could by inquiry make out its nature, it resembled water, but if upon repetition it be found really to be the product of compressed common air, then its fixed nature shews it to be a result of a very different kind to those mentioned above, and necessarily attended by far more important consequences.

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#### IV. ON THE LIQUEFACTION AND SOLIDIFICATION OF BODIES GENERALLY EXISTING AS GASES.\*

*Received December 19, 1844,—Read January 9, 1845.*

THE experiments formerly made on the liquefaction of gases,† and the results which from time to time have been added to this branch of knowledge, especially by M. THILORIER,‡ have left a constant desire on my mind to renew the investigation. This, with considerations arising out of the apparent simplicity and unity of the molecular constitution of all bodies when in

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\* [From Philosophical Transactions for 1845, Vol. 135, pp. 155-177.]

† Philosophical Transactions, 1823, pp. 160, 189.

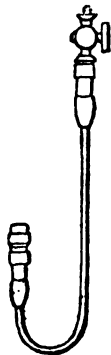
‡ Annales de Chimie, 1835, lx. 427, 432.

the gaseous or vaporous state, which may be expected, according to the indications given by the experiments of M. CAGNIARD DE LA TOUR, to pass by some simple law into their liquid state, and also the hope of seeing nitrogen, oxygen, and hydrogen, either as liquid or solid bodies, and the latter probably as a metal, have lately induced me to make many experiments on the subject, and though my success has not been equal to my desire, still I hope some of the results obtained, and the means of obtaining them, may have an interest for the Royal Society; more especially as the application of the latter may be carried much further than I as yet have had opportunity of applying them. My object, like that of some others, was to subject the gases to considerable pressure with considerable depression of temperature. To obtain the pressure, I used mechanical force, applied by two air-pumps fixed to a table. The first pump had a piston of an inch in diameter, and the second a piston of only half an inch in diameter; and these were so associated by a connecting pipe, that the first pump forced the gas into and through the valves of the second, and then the second could be employed to throw forward this gas, already condensed to ten, fifteen, or twenty atmospheres, into its final recipient at a much higher pressure.

The gases to be experimented with were either prepared and retained in gas holders or gas jars, or else, when the pumps were dispensed with, were evolved in strong glass vessels, and sent under pressure into the condensing tubes. When the gases were over water, or likely to contain water, they passed, in their way from the air-holder to the pump, through a coil of thin glass tube retained in a vessel filled with a good mixture of ice and salt, and therefore at the temperature of  $0^{\circ}$  FAHR.; the water that was condensed here was all deposited in the first two inches of the coil.

The condensing tubes were of green bottle glass, being from  $\frac{1}{8}$ th to  $\frac{1}{4}$ th of an inch external diameter, and from  $\frac{1}{12}$ d to  $\frac{1}{30}$ th of an inch in thickness. They were chiefly of two kinds, about eleven and nine inches in length; the one, when horizontal, having a curve downward near one end to dip into a cold bath, and the other, being in form like an inverted siphon, could have the bend cooled also in the same manner when necessary. Into the straight part of the horizontal tube, and the longest leg of the siphon tube, pressure gauges were introduced when required.

Fig. 1.



Caps, stop-cocks and connecting pieces were employed to attach the glass tubes to the pumps, and these, being of brass, were of the usual character of those employed for operations with gas, except that they were small and carefully made. The caps were of such size that the ends of the glass tubes entered freely into them, and had rings or a female screw worm cut in the interior,

Fig. 2.



against which the cement was to adhere. The ends of the glass tubes were roughened by a file, and when a cap was to be fastened on, both it and the end of the tube were made so warm that the cement\*, when applied, was thoroughly melted in contact with these parts, before the tube and cap were brought together and finally adjusted

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\* Five parts of resin, one part of yellow bees'-wax, and one part of red ochre, by weight, melted together.

to each other. These junctions bore a pressure of thirty, forty, and fifty atmospheres, with only one failure, in above one hundred instances; and that produced no complete separation of parts, but simply a small leak.

The caps, stop-cocks, and connectors, screwed one into the other, having one common screw thread, so as to be combined in any necessary manner. There were also screw plugs, some solid, with a male screw to close the openings or ends of caps, &c., others with a female screw to cover and close the ends of stop-cocks. All these screw joints were made tight by leaden washers; and by having these of different thickness, equal to from  $\frac{4}{8}$ th to  $\frac{12}{8}$ th of the distance between one turn of the screw thread and the next, it was easy at once to select the washer which should allow a sufficient compression in screwing up to make all air-tight, and also bring every part of the apparatus into its right position.

I have often put a pressure of fifty atmospheres into these tubes, and have had no accident or failure (except the one mentioned). With the assistance of Mr. ADDAMS I have tried their strength by a hydrostatic press, and obtained the following results:—A tube having an external diameter of 0.24 of an inch and a thickness of 0.0175 of an inch, burst with a pressure of sixty-seven atmospheres, reckoning one atmosphere as 15 lb. on the square inch. A tube which had been used, of the shape of fig. 1, its external diameter being 0.225 of an inch, and its thickness about 0.03 of an inch, sustained a pressure of 118 atmospheres without breaking, or any failure of the caps or cement, and was then removed for further use.

A tube such as I have employed for generating gases under pressure, having an external diameter of 0.6 of an inch, and a thickness of 0.035 of an inch, burst at twenty-five atmospheres.



Having these data, it was easy to select tubes abundantly sufficient in strength to sustain any force which was likely to be exerted within them in any given experiment.

The gauge used to estimate the degree of pressure to which the gas within the condensing tube was subjected was of the same kind as those formerly described,\* being a small tube of glass closed at one end with a cylinder of mercury moving in it. So the expression of ten or twenty atmospheres, means a force which is able to compress a given portion of air into  $\frac{1}{10}$ th or  $\frac{1}{20}$ th of its bulk at the pressure of one atmosphere of thirty inches of mercury. These gauges had their graduation marked on them with a black varnish, and also with Indian ink :—there are several of the gases which, when condensed, cause the varnish to liquefy, but then the Indian ink stood. For further precaution, an exact copy of the gauge was taken on paper, to be applied on the outside of the condensing tube. In most cases, when the experiment was over, the pressure was removed from the interior of the apparatus, to ascertain whether the mercury in the gauge would return back to its first or starting-place.

For the application of cold to these tubes a bath of THILORIER's mixture of solid carbonic acid and ether was used. An earthenware dish of the capacity of four cubic inches or more was fitted into a similar dish somewhat larger, with three or four folds of dry flannel intervening, and then the bath mixture was made in the inner dish. Such a bath will easily continue for twenty or thirty minutes, retaining solid carbonic acid the whole time ; and the glass tubes used would sustain sudden immersion in it without breaking.

But as my hopes of any success beyond that heretofore

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\* Philosophical Transactions, 1823, p. 192.

obtained depended more upon depression of temperature than on the pressure which I could employ in these tubes, I endeavoured to obtain a still greater degree of cold. There are, in fact, some results producible by cold which no pressure may be able to effect. Thus, solidification has not as yet been conferred on a fluid by any degree of pressure. Again, that beautiful condition which CAGNIARD DE LA TOUR has made known, and which comes on with liquids at a certain heat, may have its point of temperature for some of the bodies to be experimented with, as oxygen, hydrogen, nitrogen, &c., below that belonging to the bath of carbonic acid and ether; and, in that case, no pressure which any apparatus could bear would be able to bring them into the liquid or solid state.

To procure this lower degree of cold, the bath of carbonic acid and ether was put into an air-pump, and the air and gaseous carbonic acid rapidly removed. In this way the temperature fell so low, that the vapour of carbonic acid given off by the bath, instead of having a pressure of one atmosphere, had only a pressure of  $\frac{1}{24}$ th of an atmosphere, or 1.2 inch of mercury; for the air-pump barometer could be kept at 28.2 inches when the ordinary barometer was at 29.4. At this low temperature the carbonic acid mixed with the ether was not more volatile than water at the temperature of 86°, or alcohol at ordinary temperatures.

In order to obtain some idea of this temperature, I had an alcohol thermometer made, of which the graduation was carried below 32° FAHR., by degrees equal in capacity to those between 32° and 212°. When this thermometer was put into the bath of carbonic acid and ether surrounded by the air, but covered over with paper, it gave the temperature of 106° below 0°. When it was introduced into the bath under the air-pump, it sank to the

temperature of  $166^{\circ}$  below  $0^{\circ}$ ; or  $60^{\circ}$  below the temperature of the same bath at the pressure of one atmosphere, *i.e.* in the air. In this state the ether was very fluid, and the bath could be kept in good order for a quarter of an hour at a time.

As the exhaustion proceeded I observed the temperature of the bath and the corresponding pressure, at certain other points, of which the following may be recorded:—The external barometer was 29.4 inches:

when the mercury in the air-pump barometer was				inch.	FAHR.		
			1		the bath temperature was		
...	...	...	10	...	...	...	$-106,$
...	...	...	20	...	...	...	$-112\frac{1}{2},$
...	...	...	22	...	...	...	$-121,$
...	...	...	24	...	...	...	$-125,$
...	...	...	26	...	...	...	$-131,$
...	...	...	27	...	...	...	$-139,$
...	...	...	28	...	...	...	$-146,$
...	...	...	28.2	...	...	...	$-160,$
...	...	...		...	...	...	$-166,$

but as the thermometer takes some time to acquire the temperature of the bath, and the latter was continually falling in degree; as also the alcohol thickens considerably at the lower temperature, there is no doubt that the degrees expressed are not so low as they ought to be, perhaps even by  $5^{\circ}$  or  $6^{\circ}$  in most cases.

With *dry* carbonic acid under the air-pump receiver I could raise the pump barometer to twenty-nine inches when the external barometer was at thirty inches.

The arrangement by which this cooling power was combined in its effect on gases with the pressure of the pumps, was very simple in principle. An air-pump receiver open at the top was employed; the brass plate which closed the aperture had a small brass tube about six inches long, passing through it air-tight by means of a stuffing-box, so as to move easily up and down in a vertical direction. One of the glass condensing siphon tubes, already described, fig. 1, was screwed on to the lower end of the sliding tube, and the upper end of the

latter was connected with a communicating tube in two lengths, reaching from it to the condensing pumps ; this tube was small, of brass, and  $9\frac{1}{2}$  feet in length ; it passed six inches horizontally from the condensing pumps, then rose vertically for two feet, afterwards proceeded horizontally for seven feet, and finally turned down and was immediately connected with the sliding tube. By this means the latter could be raised and lowered vertically, without any strain upon the connections, and the condensing tube lowered into the cold bath *in vacuo*, or raised to have its contents examined at pleasure. The capacity of the connecting tubes beyond the last condensing pump was only two cubic inches.

When experimenting with any particular gas, the apparatus was put together fast and tight, except the solid terminal screw-plug at the short end of the condensing tube, which being the very extremity of the apparatus, was left a little loose. Then, by the condensing pumps, abundance of gas was passed through the apparatus to sweep out every portion of air, after which the terminal plug was screwed up, the cold bath arranged, and the combined effects of cold and pressure brought to unite upon the gas.

There are many gases which condense at less than the pressure of one atmosphere when submitted to the cold of a carbonic acid bath in air (which latter can upon occasions be brought considerably below —  $106^{\circ}$  FAHR.). These it was easy, therefore, to reduce, by sending them through small conducting tubes into tubular receivers placed in the cold bath. When the receivers had previously been softened in a spirit lamp flame, and narrow necks formed on them, it was not difficult by a little further management, hermetically to seal up these substances in their condensed state. In this manner chlorine, cyanogen, ammonia, sulphuretted hydrogen, arseniuretted

hydrogen, hydriodic acid, hydrobromic acid, and even carbonic acid, were obtained, sealed up in tubes in the liquid state; and euchlorine was also secured in a tube receiver with a cap and screw-plug. By using a carbonic acid bath, first cooled *in vacuo*, there is no doubt other condensed gases could be secured in the same way.

The fluid carbonic acid was supplied to me by Mr. ADDAMS, in his perfect apparatus, in portions of about 220 cubic inches each. The solid carbonic acid, when produced from it, was preserved in a glass; itself retained in the middle of three concentric glass jars, separated from each other by dry jackets of woollen cloth. So effectual was this arrangement, that I have frequently worked for a whole day of twelve and fourteen hours, having solid carbonic acid in the reservoir, and enough for all the baths I required during the whole time, produced by one supply of 220 cubic inches.\*

By the apparatus, and in the manner, now described, all the gases before condensed were very easily reduced, and some new results were obtained. When a gas was liquefied, it was easy to close the stop-cock; and then remove the condensing tube with the fluid from the rest of the apparatus. But in order to preserve the liquid from escaping as gas, a further precaution was necessary; namely, to cover over the exposed end of the stop-cock by a blank female screw-cap and leaden washer, and also

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\* On one occasion the solid carbonic acid was exceedingly electric, but I could not produce the effect again: it was probably connected with the presence of oil which was in the carbonic acid box; neither it nor the filaments of ice which formed on it in the air conducted, for when touched it preserved its electric state. Believing as yet that the account I have given of the cause of the electric state of an issuing jet of steam and water (Phil. Trans. 1843, p. 17) is the true one, I conclude that this also was a case of the production of electricity simply by friction, and unconnected with vaporization.

to tighten perfectly the screw of the stop-cock plug. With these precautions I have kept carbonic acid, nitrous oxide, fluosilicon, &c., for several days.

Even with gases which could be condensed by the carbonic acid bath in air, this apparatus in the air-pump had, in one respect, the advantage; for when the condensing tube was lifted out of the bath into the air, it immediately became covered with hoar frost, obscuring the view of that which was within; but *in vacuo* this was not the case, and the contents of the tube could be very well examined by the eye.

*Olefant gas*.—This gas condensed into a clear, colourless, transparent fluid, but did not become solid even in the carbonic acid bath *in vacuo*; whether this was because the temperature was not low enough, or for other reasons referred to in the account of euchlorine, is uncertain.

The pressure of the vapour of this substance at the temperature of the carbonic acid bath in air ( $-103^{\circ}$  FAHR.) appeared singularly uncertain, being on different occasions, and with different specimens, 3.7, 8.7, 5 and 6 atmospheres. The Table below shows the tension of vapour for certain degrees below  $0^{\circ}$  FAHR., with two different specimens obtained at different times, and it will illustrate this point.

FAHR.		Atmospheres.		Atmospheres.
—100	. .	4.60	. .	9.30
—90	. .	5.68	. .	10.26
—80	. .	6.92	. .	11.33
—70	. .	8.32	. .	12.52
—60	. .	9.88	. .	13.86
—50	. .	11.72	. .	15.36
—40	. .	13.94	. .	17.05
—30	. .	16.56	. .	18.98
—20	. .	19.58	. .	21.23
—10	. .	. .	. .	23.89
0	. .	. .	. .	27.18
10	. .	. .	. .	31.70
20	. .	. .	. .	36.80
30	. .	. .	. .	42.50

I have not yet resolved this irregularity, but believe there are two or more substances, physically, and perhaps occasionally chemically different, in olefiant gas; and varying in proportion with the circumstances of heat, proportions of ingredients, &c., attending the preparation.

The fluid affected the resin of the gauge graduation, and probably also the resin of the cap cement, though slowly.

*Hydriodic acid.*—This substance was prepared from the iodide of phosphorus by heating it with a very little water. It is easily condensable by the temperature of a carbonic acid bath; it was redistilled, and thus obtained perfectly pure.

The acid may be obtained either in the solid or liquid, or (of course) in the gaseous state. As a solid it is perfectly clear, transparent, and colourless; having fissures or cracks in it resembling those that run through ice. Its solidifying temperature is nearly  $-60^{\circ}$  FAHR., and then its vapour has not the pressure of one atmosphere; at a point a little higher it becomes a clear liquid, and this point is close upon that which corresponds to a vaporous pressure of one atmosphere. The acid dissolves the cap cement and the bitumen of the gauge graduation; and appears also to dissolve and act on fat, for it leaked by the plug of the stop-cock with remarkable facility. It acts on the brass of the apparatus, and also on the mercury in the gauge. Hence the following results as to pressures and temperatures are not to be considered more than approximations:—

At  $0^{\circ}$  FAHR. pressure was 2.9 atmospheres.

At  $32^{\circ}$  FAHR. pressure was 3.97 atmospheres.

At  $60^{\circ}$  FAHR. pressure was 5.86 atmospheres.

*Hydrobromic acid.*—This acid was prepared by adding

to perbromide of phosphorus\* about one-third of its bulk of water in a proper distillatory apparatus formed of glass tube, and then applying heat to distil off the gaseous acid. This being sent into a very cold receiver, was condensed into a liquid, which being rectified by a second distillation, was then experimented with.

Hydrobromic acid condenses into a clear colourless liquid at  $100^{\circ}$  below  $0^{\circ}$ , or lower, and has not the pressure of one atmosphere at the temperature of the carbonic acid bath in air. It soon obstructs and renders the motion of the mercury in the air-gauge irregular, so that I did not obtain a measure of its elastic force; but it is less than that of muriatic acid. At and below the temperature of  $-124^{\circ}$  FAHR. it is a solid, transparent, crystalline body. It does not freeze until reduced much lower than this temperature; but being frozen by the carbonic acid bath *in vacuo*, it remains a solid until the temperature in rising attains to  $-124^{\circ}$ .

*Fluosilicon.*—I found that this substance in the gaseous state might be brought in contact with the oil and metal of the pumps, without causing injury to them, for a time sufficiently long to apply the joint process of condensation already described. The substance liquefied under a pressure of about nine atmospheres at the lowest temperature, or at  $160^{\circ}$  below  $0^{\circ}$ ; and was then clear, transparent, colourless, and very fluid like hot ether. It did not solidify at any temperature to which I could submit it. I was able to preserve it in the tube until the

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\* The bromides of phosphorus are easily made without risk of explosion. If a glass tube be bent so as to have two depressions, phosphorus placed in one and bromine in the other; then by inclining the tube, the vapour of bromine can be made to flow gradually on to, and combine with, the phosphorus. The fluid protobromide is first formed, and this is afterwards converted into solid perbromide. The excess of bromine may be dissipated by the careful application of heat.



next day. Some leakage had then taken place (for it ultimately acted on the lubricating fat of the stop-cock), and there was no liquid in the tube at common temperatures; but when the bend of the tube was cooled to  $32^{\circ}$  by a little ice, fluid appeared: a bath of ice and salt caused a still more abundant condensation. The pressure appeared then to be above thirty atmospheres, but the motion of the mercury in the gauge had become obstructed through the action of the fluosilicon, and no confidence could be reposed in its indications.

*Phosphuretted hydrogen.*—This gas was prepared by boiling phosphorus in a strong pure solution of caustic potassa, and the gas was preserved over water in a dark room for several days to cause the deposition of any mere vapour of phosphorus which it might contain. It was then subjected to high pressure in a tube cooled by a carbonic acid bath, which had itself been cooled under the receiver of the air-pump. The gas in its way to the pumps passed through a long spiral of thin narrow glass tube immersed in a mixture of ice and salt at  $0^{\circ}$ , to remove as much water from it as possible.

By these means the phosphuretted hydrogen was liquefied; for a pure, clear, colourless, transparent and very limpid fluid appeared, which could not be solidified by any temperature applied, and which when the pressure was taken off immediately rose again in the form of gas. Still the whole of the gas was not condensable into this fluid. By working the pumps the pressure would rise up to twenty-five atmospheres at this very low temperature, and yet at the pressure of two or three atmospheres and the same temperature, liquid would remain. There can be no doubt that phosphuretted hydrogen condensed, but neither can there be a doubt that some other gas, not so condensable, was also present, which perhaps may be either another phosphuretted hydrogen or hydrogen itself.

*Fluoboron.*—This substance was prepared from fluor spar, fused boracic acid and strong sulphuric acid, in a tube generator such as that already described, and conducted into a condensing tube under the generating pressure. The ordinary carbonic acid bath did not condense it, but the application of one cooled under the air-pump caused its liquefaction, and fluoboron then appeared as a very limpid, colourless, clear fluid, showing no signs of solidification, but when at the lowest temperature mobile as hot ether. When the pressure was taken off, or the temperature raised, it returned into the state of gas.

The following are some results of pressure, all that I could obtain with the liquid in my possession; for, as the liquid is light and the gas heavy, the former rapidly disappears in producing the latter. They make no pretensions to accuracy, and are given only for general information.

FAHR.	Atmospheres.	FAHR.	Atmospheres.	FAHR.	Atmospheres.
—100 . .	4.61	—72 . .	9.23	—62 . .	11.54
—82 . .	7.5	—66 . .	10.00		

The preceding are, as far as I am aware, new results of the liquefaction and solidification of gases. I will now briefly add such other information respecting solidification, pressure, &c., as I have obtained with gaseous bodies previously condensed. As to pressure, considerable irregularity often occurred, which I cannot always refer to its true cause; sometimes a little of the compressed gas would creep by the mercury in the gauge, and increase the volume of inclosed air; and this varied with different substances, probably by some tendency which the glass had to favour the condensation of one (by

something analogous to hygrometric action) more than another. But even when the mercury returned to its place in the gauge, there were anomalies which seemed to imply, that a substance, supposed to be one, might be a mixture of two or more. It is, of course, essential that the gauge be preserved at the same temperature throughout the observations.

*Muriatic acid.*—This substance did not freeze at the lowest temperature to which I could attain. Liquid muriatic acid dissolves bitumen; the solution, liberated from pressure, boils, giving off muriatic acid vapour, and the bitumen is left in a solid frothy state, and probably altered, in some degree, chemically. The acid unites with and softens the resinous cap cement, but leaves it when the pressure is diminished. The following are certain pressures and temperatures which, I believe, are not very far from truth; the marked numbers are from experiment.

FAHR.	Atmospheres.	FAHR.	Atmospheres.	FAHR.	Atmospheres.
—100 .	1.80	—53 .	5.83	—5 .	13.88
—92 .	2.28	—50 .	6.30	0 .	15.04
—90 .	2.38	—42 .	7.40	10 .	17.74
—83 .	2.90	—40 .	7.68	20 .	21.09
—80 .	3.12	—33 .	8.53	25 .	23.08
—77 .	3.37	—30 .	9.22	30 .	25.32
—70 .	4.02	—22 .	10.66	32 .	26.20
—67 .	4.26	—20 .	10.92	40 .	30.67
—60 .	5.08	—10 .	12.82		

The result formerly obtained\* was forty atmospheres at the temperature of 50° FAHR.

*Sulphurous acid.*—When liquid, it dissolves bitumen. It becomes a crystalline, transparent, colourless, solid body, at —105° FAHR.; when partly frozen the crystals are well-formed. The solid sulphurous acid is heavier than the liquid, and sinks freely in it. The following is

\* Philosophical Transactions, 1823, p. 198.

a table of pressures in atmospheres of 30 inches mercury, of which the marked results are from many observations, the others are interpolated. They differ considerably from the results obtained by BUNSEN,\* but agree with my first and only result.

FAHR.	Atmospheres	FAHR.	Atmospheres.	FAHR.	Atmospheres.
0	.	0	.	0	.
10	. . 0.725	40	. . 1.78	76.8	. . 3.50
14	. . 0.92	46.5	. . 2.00	85	. . 4.00
19	. . 1.00	48	. . 2.06	90	. . 4.35
23	. . 1.12	56	. . 2.42	93	. . 4.50
26	. . 1.23	58	. . 2.50	98	. . 5.00
31.5	. . 1.33	64	. . 2.76	100	. . 5.16
32	. . 1.50	68	. . 3.00	104	. . 5.50
33	. . 1.53	73.5	. . 3.28	110	. . 6.00
33	. . 1.57				

*Sulphuretted hydrogen.*—This substance solidifies at 122° FAHR. below 0°, and is then a white crystalline translucent substance, not remaining clear and transparent in the solid state like water, carbonic acid, nitrous oxide, &c., but forming a mass of confused crystals like common salt or nitrate of ammonia, solidified from the melted state. As it fuses at temperatures above —122°, the solid part sinks freely in the fluid, indicating that it is considerably heavier. At this temperature the pressure of its vapour is less than one atmosphere, not more, probably, than 0.8 of an atmosphere, so that the liquid allowed to evaporate in the air would not solidify as carbonic acid does.

The following is a table of the tension of its vapour, the marked numbers being close to experimental results, and the rest interpolated. The curve resulting from these numbers, though coming out nearly identical in different series of experiments, is apparently so different in its character from that of water or carbonic acid, as to leave doubts on my mind respecting it, or else of the

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\* Bibliothèque Universelle, 1839, xxiii. p. 185.

identity of every portion of the fluid obtained, yet the crystallization and other characters of the latter seemed to show that it was a pure substance.

FAHR.	Atmospheres.	FAHR.	Atmospheres.	FAHR.	Atmospheres.
—100 . .	1.02	—50 . .	2.35	0 . .	6.10
✓—94 . .	1.09	✓—45 . .	2.59	10 . .	7.21
✓—90 . .	1.15	✓—40 . .	2.86	20 . .	8.44
✓—83 . .	1.27	—30 . .	3.49	✓26 . .	9.36
—80 . .	1.33	✓—24 . .	3.95	30 . .	9.94
✓—74 . .	1.50	✓—20 . .	4.24	40 . .	11.84
—70 . .	1.59	✓—16 . .	4.60	✓48 . .	13.70
✓—68 . .	1.67	—10 . .	5.11	50 . .	14.14
—60 . .	1.93	✓—2 . .	5.90	✓52 . .	14.60
✓—58 . .	2.00				

*Carbonic acid.*—The solidification of carbonic acid by M. THILORIER is one of the most beautiful experimental results of modern times. He obtained the substance, as is well known, in the form of a concrete white mass like fine snow, aggregated. When it is melted and resolidified by a bath of low temperature, it then appears as a clear, transparent, crystalline, colourless body, like ice; so clear, indeed, that at times it was doubtful to the eye whether anything was in the tube, yet at the same time the part was filled with solid carbonic acid. It melts at the temperature of  $-70^{\circ}$  or  $-72^{\circ}$  FAHR., and the solid carbonic acid is heavier than the fluid bathing it. The solid or liquid carbonic acid at this temperature has a pressure of 5.33 atmospheres nearly. Hence it is easy to understand the readiness with which liquid carbonic acid, when allowed to escape into the air, exerting only a pressure of one atmosphere, freezes a part of itself by the evaporation of another part.

THILORIER gives  $-100^{\circ}$  C. or  $-148^{\circ}$  FAHR. as the temperature at which carbonic acid becomes solid. This however is rather the temperature to which solid carbonic acid can sink by further evaporation in the air, and is a temperature belonging to a pressure, not only lower than

that of 5.33 atmospheres, but even much below that of one atmosphere. This cooling effect to temperatures below the boiling-point often appears. A bath of carbonic acid and ether exposed to the air will cool a tube containing condensed solid carbonic acid, until the pressure within the tube is less than one atmosphere; yet, if the same bath be covered up so as to have the pressure of one atmosphere of carbonic acid vapour over it, then the temperature is such as to produce a pressure of 2.5 atmospheres by the vapour of the solid carbonic acid within the tube.

The estimates of the pressure of carbonic acid vapour are sadly at variance; thus, THILORIER\* says it has a pressure of 26 atmospheres at  $-4^{\circ}$  FAHR., whilst ADDAMS† says that for that pressure it requires a temperature of  $30^{\circ}$ . ADDAMS gives the pressure about  $27\frac{1}{2}$  atmospheres at  $32^{\circ}$ , but THILORIER and myself‡ give it as 36 atmospheres at the same temperature. At  $50^{\circ}$  BRUNEL§ estimates the pressure as 60 atmospheres, whilst ADDAMS makes it only 34.67 atmospheres. At  $86^{\circ}$  THILORIER finds the pressure to be 73 atmospheres; at  $4^{\circ}$  more, or  $90^{\circ}$ , BRUNEL makes it 120 atmospheres; and at  $10^{\circ}$  more, or  $100^{\circ}$ , ADDAMS makes it less than THILORIER at  $86^{\circ}$ , and only 62.32 atmospheres; even at  $150^{\circ}$  the pressure with him is not quite 100 atmospheres.

I am inclined to think that at about  $90^{\circ}$  CAGNIARD DE LA TOUR's state comes on with carbonic acid. From THILORIER's data we may obtain the specific gravity of the liquid and the vapour over it at the temperature of  $86^{\circ}$  FAHR., and the former is little more than twice that of the latter; hence a few degrees more of temperature

\* *Annales de Chimie*, 1835, ix. 427, 432.

† Report of British Association, 1838, p. 70.

‡ *Philosophical Transactions*, 1823, p. 193.

§ *Royal Institution Journal*, xxi. 132.

would bring them together, and BRUNEL's result seems to imply that the state was then on, but in that case ADDAMS's results could only be accounted for by supposing that there was a deficiency of carbonic acid. The following are the pressures which I have recently obtained :—

FAHR.	Atmospheres.	FAHR.	Atmospheres.	FAHR.	Atmospheres
—111 . .	1.14	—60 . .	6.97	— 4 . .	21.48
—110 . .	1.17	—56 . .	7.70	0 . .	22.84
—107 . .	1.36	—50 . .	8.88	5 . .	24.75
—100 . .	1.85	—40 . .	11.07	10 . .	26.82
— 95 . .	2.28	—34 . .	12.50	15 . .	29.09
— 90 . .	2.77	—30 . .	13.54	20 . .	30.65
— 83 . .	3.60	—23 . .	15.45	23 . .	33.15
— 80 . .	3.93	—20 . .	16.30	30 . .	37.19
— 75 . .	4.60	—15 . .	17.80	32 . .	38.50
— 70 . .	5.33	—10 . .	19.38		

Carbonic acid is remarkable amongst bodies for the high tension of the vapour which it gives off whilst in the solid or glacial state. There is no other substance which at all comes near it in this respect, and it causes an inversion of what in all other cases is the natural order of events. Thus, if, as is the case with water, ether, mercury or any other fluid, that temperature at which carbonic acid gives off vapour equal in elastic force to one atmosphere, be called its boiling-point ; or, if (to produce the actual effect of ebullition) the carbonic acid be plunged below the surface of alcohol or ether, then we shall perceive that the freezing and boiling-points are inverted, i.e. that the freezing-point is the hotter, and the boiling-point the colder of the two, the latter being about 50° below the former.

*Euchlorine.* — This substance was easily converted from the gaseous state into a solid crystalline body, which, by a little increase of temperature, melted into an orange-red fluid, and by diminution of temperature again congealed ; the solid euchlorine had the colour and

general appearance of bichromate of potassa ; it was moderately hard, brittle and translucent ; and the crystals were perfectly clear. It melted at the temperature of  $75^{\circ}$  below  $0^{\circ}$ , and the solid portion was heavier than the liquid.

When in the solid state it gives off so little vapour that the eye is not sensible of its presence by any degree of colour in the air over it when looking down a tube four inches in length, at the bottom of which is the substance. Hence the pressure of its vapour at that temperature must be very small.

Some hours after, wishing to solidify the same portion of euchlorine which was then in a liquid state, I placed the tube in a bath at  $-110^{\circ}$ , but could not succeed either by continuance of the tube in the bath, or shaking the fluid in the tube, or opening the tube to allow the full pressure of the atmosphere ; but when the liquid euchlorine was touched by a platinum wire it instantly became solid, and exhibited all the properties before described. There are many similar instances amongst ordinary substances, but the effect in this case makes me hesitate in concluding that all the gases which as yet have refused to solidify at temperatures as low as  $166^{\circ}$  below  $0^{\circ}$ , cannot acquire the solid state at such a temperature.

*Nitrous oxide.*—This substance was obtained *solid* by the temperature of the carbonic acid bath *in vacuo*, and appeared as a beautiful clear crystalline colourless body. The temperature required for this effect must have been very nearly the lowest, perhaps about  $150^{\circ}$  below  $0^{\circ}$ . The pressure of the vapour rising from the solid nitrous oxide was less than one atmosphere.

Hence it was concluded that liquid nitrous oxide could not freeze itself by evaporation at one atmosphere, as carbonic acid does ; and this was found to be true, for when a tube containing much liquid was freely opened,



so as to allow evaporation down to one atmosphere, the liquid boiled and cooled itself, but remained a liquid. The cold produced by the evaporation was very great, and this was shown by putting the part of the tube containing the liquid nitrous oxide, into a cold bath of carbonic acid, for the latter was like a hot bath to the former, and instantly made it boil rapidly.

I kept this substance for some weeks in a tube closed by stop-cocks and cemented caps. In that time there was no action on the bitumen of the graduation, nor on the cement of the caps; these bodies remained perfectly unaltered.

Hence it is probable that this substance may be used in certain cases, instead of carbonic acid, to produce degrees of cold far below those which the latter body can supply. Down to a certain temperature, that of its solidification, it would not even require ether to give contact, and below that temperature it could easily be used mingled with ether; its vapour would do no harm to an air-pump, and there is no doubt that the substance placed *in vacuo* would acquire a temperature lower than any as yet known, perhaps as far below the carbonic acid bath *in vacuo* as that is below the same bath in air.

This substance, like olefiant gas, gave very uncertain results at different times as to the pressure of its vapour; results which can only be accounted for by supposing that there are two different bodies present, soluble in each other, but differing in the elasticity of their vapour. Four different portions gave at the same temperature, namely,  $-106^{\circ}$  FAHR., the following great differences in pressure, 1.66; 4.4; 5.0; and 6.3 atmospheres, and this after the elastic atmosphere left in the tubes at the conclusion of the condensation had been allowed to escape, and be replaced by a portion of the respective liquids which then rose in vapour. The following Table gives

certain results with a portion of liquid which exerted a pressure of six atmospheres at  $-106^{\circ}$  FAHR.

FAHR.		Atmospheres.	Atmospheres.
—40	. .	10.20	
—35	. .	10.95	
—30	. .	11.80	
—25	. .	12.75	
—20	. .	13.80	
—15	. .	14.95	
—10	. .	16.20	
— 5	. .	17.55	
0	. .	19.05	. . 24.40
5	. .	20.70	. . 26.08
10	. .	22.50	. . 27.84
15	. .	24.45	. . 29.68
20	. .	26.55	. . 31.62
25	. .	28.85	. . 33.66
30	. .		. . 35.82
35	. .		. . 38.10

The second column expresses the pressures given as the fluid was raised from low to higher temperatures. The third column shows the pressures given the next day with the same tube after it had attained to and continued at the atmospheric temperature for some hours. There is a difference of four or five atmospheres between the two, showing that in the first instance the previous low temperature had caused the solution of a more volatile part in the less volatile and liquid portion, and that the prolonged application of a higher temperature during the night had gradually raised it again in vapour. This result occurred again and again with the same specimen.\*

*Cyanogen.* — This substance becomes a solid trans-

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\* This substance is one of those which I liquefied in 1823 (see Philosophical Transactions). Since writing the above I perceive that M. NATTERER has condensed it into the liquid state by the use of pumps only (see Comptes Rendus, 1844, 18th Nov. p. 1111), and obtained the liquid in considerable quantities. The non-solidification of it by exposure to the air perfectly accords with my own results.

parent crystalline body, as BUNSEN has already stated,\* which raised to the temperature of  $-30^{\circ}$  FAHR. then liquefies. The solid and liquid appear to be nearly of the same specific gravity, but the solid is perhaps the denser of the two.

The mixed solid and liquid substance yields a vapour of rather less pressure than one atmosphere. In accordance with this result, if the liquid be exposed to the air, it does not freeze itself as carbonic acid does.

The liquid tends to distil over and condense on the cap cement and bitumen of the gauge, but only slightly. When cyanogen is made from cyanide of mercury sealed up hermetically in a glass tube, the cyanogen distils back and condenses in the paracyanic residue of the distillation, but the pressure of the vapour at common temperatures is still as great, or very nearly so, as if the cyanogen were in a clean separate liquid state.

A measured portion of liquid cyanogen was allowed to escape and expand into gas. In this way one volume of liquid at the temperature of  $63^{\circ}$  FAHR. gave 393.9 volumes of gas at the same temperature and the barometric pressure of 30.2 inches. If 100 cubic inches of the gas be admitted to weigh 55.5 grains, then a cubic inch of the liquid would weigh 218.6 grains. This gives its specific gravity as 0.866. When first condensed I estimated it as nearly 0.9.

Cyanogen is a substance which yielded on different occasions results of vaporous tension differing much from each other, though the substance appeared always to be pure. The following are numbers in which I place some confidence, the pressures being in atmospheres of 30 inches of mercury, and the marked results experimental.†

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\* Bibliothèque Universelle, 1839, xxiii. p. 184.

† See BUNSEN's results, Bibliothèque Universelle, 1839, xxiii. p. 185.

FAHR.	Atmospheres.	FAHR.	Atmospheres.	FAHR.	Atmospheres.
0 . .	1.25	38.5 . .	2.72	77 . .	5.00
8.5 . .	1.5	44.5 . .	3.00	79 . .	5.16
10 . .	1.53	48 . .	3.17	83 . .	5.50
15 . .	1.72	50 . .	3.28	88.3 . .	6.00
20 . .	1.89	52 . .	3.36	93.5 . .	6.50
22.8 . .	2.00	54.3 . .	3.50	95 . .	6.64
27 . .	2.20	63 . .	4.00	98.4 . .	7.00
32 . .	2.37	70 . .	4.50	103 . .	7.50
34.5 . .	2.50	74 . .	4.79		

*Ammonia*.—This body may be obtained as a *solid*, white, translucent, crystalline substance, melting at the temperature of  $103^{\circ}$  below  $0^{\circ}$ ; at which point the solid substance is heavier than the liquid. In that state the pressure of its vapour must be very small.

Liquid ammonia at  $60^{\circ}$  was allowed to expand into ammoniacal gas at the same temperature; one volume of the liquid gave 1009.8 volumes of the gas, the barometer being at the pressure of 30.2 inches. If 100 cubic inches of ammoniacal gas be allowed to weigh 18.28 grains, it will give 184.6 grains as the weight of a cubic inch of liquid ammonia at  $60^{\circ}$ . Hence its specific gravity at that temperature will be 0.731. In the old experiments I found by another kind of process that its specific gravity was 0.76 at  $50^{\circ}$ .

The following is a table of the pressure of ammonia vapour, the marked results, as before, being those obtained by experiment:—

FAHR.	Atmospheres.	FAHR.	Atmospheres.	FAHR.	Atmospheres.
0 . .	2.48	41 . .	5.10	61.3 . .	7.00
0.5 . .	2.50	44 . .	5.36	65.6 . .	7.50
9.3 . .	3.00	45 . .	5.45	67 . .	7.63
18 . .	3.50	45.8 . .	5.50	69.4 . .	8.00
21 . .	3.72	49 . .	5.83	73 . .	8.50
25.8 . .	4.00	51.4 . .	6.00	76.8 . .	9.00
26 . .	4.04	52 . .	6.10	80 . .	9.50
32 . .	4.44	55 . .	6.38	83 . .	10.00
33 . .	4.50	56.5 . .	6.50	85 . .	10.30
39.5 . .	5.00	60 . .	6.90		

**Arseniuretted Hydrogen.**—This body, liquefied by DUMAS and SOUBEIRAN, did not solidify at the lowest temperature to which I could submit it, i.e. not at  $166^{\circ}$  below  $0^{\circ}$  FAHR. In the following table of the elasticity of its vapour the marked results are experimental, and the others interpolated:—

FAHR.	Atmospheres.	FAHR.	Atmospheres.	FAHR.	Atmospheres.
$0^{\circ}$		$0^{\circ}$		$0^{\circ}$	
$\sim 75$ . .	0.94	$\sim 30$ . .	2.84	$\sim 10$ . .	6.24
$\sim 70$ . .	1.08	$\sim 23$ . .	3.32	$\sim 20$ . .	7.39
$\sim 64$ . .	1.26	$\sim 20$ . .	3.51	$30$ . .	8.66
$\sim 60$ . .	1.40	$\sim 10$ . .	4.30	$\sim 32$ . .	8.95
$\sim 52$ . .	1.73	$\sim 5$ . .	4.74	$\sim 40$ . .	10.05
$\sim 50$ . .	1.80	$\sim 0$ . .	5.21	$\sim 50$ . .	11.56
$\sim 40$ . .	2.28	$\sim 3$ . .	5.56	$\sim 60$ . .	13.19
$\sim 36$ . .	2.50				

The following bodies would not freeze at the very low temperature of the carbonic acid bath *in vacuo* ( $-166^{\circ}$  FAHR.):—Chlorine, ether, alcohol, sulphuret of carbon, caoutchoucine, camphine or rectified oil of turpentine. The alcohol, caoutchoucine, and camphine lost fluidity and thickened somewhat at  $-106^{\circ}$ , and still more at the lower temperature of  $-166^{\circ}$ . The alcohol then poured from side to side like an oil.

Dry yellow fluid nitrous acid when cooled below  $0^{\circ}$  loses the greater part of its colour, and then fuses into a white, crystalline, brittle and but slightly translucent substance, which fuses a little above  $0^{\circ}$  FAHR. The green and probably hydrated acid required a much lower temperature for its solidification, and then became a pale bluish solid. There were then evidently two bodies, the dry acid which froze out first, and then the hydrate, which requires at least  $-30^{\circ}$  below  $0^{\circ}$  before it will solidify.

The following gases showed no signs of liquefaction

when cooled by the carbonic acid bath *in vacuo*, even at the pressures expressed :—

	Atmospheres.
Hydrogen at . . . . .	27
Oxygen at . . . . .	27
Nitrogen at . . . . .	50
Nitric oxide at . . . . .	50
Carbonic oxide at . . . . .	40
Coal gas . . . . .	32

The difference in the facility of leakage was one reason of the difference in the pressure applied. I found it impossible, from this cause, to raise the pressure of hydrogen higher than twenty-seven atmospheres by an apparatus that was quite tight enough to confine nitrogen up to double that pressure.

M. CAGNIARD DE LA TOUR has shown that at a certain temperature, a liquid, under sufficient pressure, becomes clear transparent vapour or gas, having the same bulk as the liquid. At this temperature, or one a little higher, it is not likely that any increase of pressure, except perhaps one exceedingly great, would convert the gas into a liquid. Now the temperature of  $166^{\circ}$  below  $0^{\circ}$ , low as it is, is probably *above* this point of temperature for hydrogen, and perhaps for nitrogen and oxygen, and then no compression without the conjoint application of a degree of cold below that we have as yet obtained, can be expected to take from them their gaseous state. Further, as ether assumes this state before the pressure of its vapour has acquired thirty-eight atmospheres, it is more than probable that gases which can resist the pressure of from twenty-seven to fifty atmospheres at a temperature of  $166^{\circ}$  below  $0^{\circ}$  could never appear as liquids, or be made to lose their gaseous state at common temperatures. They may probably be brought into the state of very condensed gases, but not liquefied.

Some very interesting experiments on the compression

of gases have been made by M. G. AIME,\* in which oxygen, olefiant, nitric oxide, carbonic oxide, fluosilicon, hydrogen, and nitrogen gases were submitted to pressures, rising up to 220 atmospheres in the case of the two last ; but this was in the depths of the sea where the results under pressure could not be examined. Several of them were diminished in bulk in a ratio far greater than the pressure put upon them ; but both M. CAGNIARD DE LA TOUR and M. THILORIER have shown that this is often the case whilst the substance retains the gaseous form. It is possible that olefiant gas and fluosilicon may have liquefied down below, but they have not yet been seen in the liquid state except in my own experiments, and in them not at temperatures above 40° FAHR. The results with oxygen are so unsteady and contradictory as to cause doubt in regard to those obtained with the other gases by the same process.

Thus, though as yet I have not condensed oxygen, hydrogen, or nitrogen, the original objects of my pursuit, I have added six substances, usually gaseous, to the list of those that could previously be shown in the liquid state, and have reduced seven, including ammonia, nitrous oxide, and sulphuretted hydrogen, into the solid form. And though the numbers expressing tension of vapour cannot (because of the difficulties respecting the use of thermometers and the apparatus generally) be considered as exact, I am in hopes they will assist in developing some general law governing the vaporization of all bodies, and also in illustrating the physical state of gaseous bodies as they are presented to us under ordinary temperature and pressure.

*Royal Institution,*

*Nov. 15, 1844.*

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\* *Annales de Chimie*, 1843, viii. 275.

NOTE.—*Additional remarks respecting the Condensation of Gases.*

*Received February 20,—Read February 20, 1845.*

*Nitrous oxide.*—Suspecting the presence on former occasions of nitrogen in the nitrous oxide, and mainly because of muriate in the nitrate of ammonia used, I prepared that salt in a pure state from nitric acid and carbonate of ammonia previously proved, by nitrate of silver, to be free from muriatic acid. After the nitrous oxide prepared from this salt had remained for some days in well-closed bottles in contact with a little water, I condensed it in the manner already described, and when condensed I allowed half the fluid to escape in vapour, that as much as possible of the less condensable portion might be carried off. In this way as much gas as would fill the capacity of the vessels twenty or thirty times or more was allowed to escape. Afterwards the following series of pressures was obtained :—

FAHR.	Atmospheres.	FAHR.	Atmospheres.	FAHR.	Atmospheres.
—125 . .	1.00	—70 . .	4.11	—15 . .	14.69
—120 . .	1.10	—65 . .	4.70	—10 . .	16.15
—115 . .	1.22	—60 . .	5.36	— 5 . .	17.70
—110 . .	1.37	—55 . .	6.09	0 . .	19.34
—105 . .	1.55	—50 . .	6.89	5 . .	21.07
—100 . .	1.77	—45 . .	7.76	10 . .	22.89
— 95 . .	2.03	—40 . .	8.71	15 . .	24.80
— 90 . .	2.34	—35 . .	9.74	20 . .	26.80
— 85 . .	2.70	—30 . .	10.85	25 . .	28.90
— 80 . .	3.11	—25 . .	12.04	30 . .	31.10
— 75 . .	3.58	—20 . .	13.32	35 . .	33.40

These numbers may all be taken as the results of experiments. Where the temperatures are not those actually observed, they are in almost all cases within a degree of it, and proportionate to the effects really observed. The departure of the real observations from the numbers given is very small. This table I consider as far more



worthy of confidence than the former, and yet it is manifest that the curve is not consistent with the idea of a pure single substance, for the pressures at the lowest temperature are too high. I believe that there are still two bodies present, and that the more volatile, as before said, is condensable in the liquid of the less volatile; but I think there is a far smaller proportion of the more volatile (nitrogen, or whatever it may be) than in the former case.

*Olefiant gas.*—The olefiant gas condensed in the former experiment was prepared in the ordinary way, using excellent alcohol and sulphuric acid; then washed by agitation with about half its bulk of water, and finally left for three days over a thick mixture of lime and water with occasional agitation. In this way all the sulphurous and carbonic acids were removed, and I believe all the ether, except such minute portions as could not interfere with my results. In respect of the ether, I have since found that the process is satisfactory; for when I purposely added ether vapour to air, so as to increase its bulk by one-third, treatment like that above removed it, so as to leave the air of its original volume. There was yet a slight odour of ether left, but not so much as that conferred by adding one volume of the vapour of ether to 1200 or 1500 volumes of air. I find that when air is expanded  $\frac{1}{4}$ th or  $\frac{1}{3}$ rd more by the addition of the vapour of ether, washing first of all with about  $\frac{1}{10}$ th of its volume of water, then again with about as much water, and lastly with its volume of water, removes the ether to such a degree, that though a little smell may remain, the air is of its original volume.

As already stated, it is the presence of other and more volatile hydrocarbons than olefiant gas, which the tensions obtained seemed to indicate, both in the gas and the liquid resulting from its condensation. In a

further search after these I discovered a property of olefiant gas which I am not aware is known (since I do not find it referred to in books), namely its ready solubility in strong alcohol, ether, oil of turpentine, and such like bodies.\* Alcohol will take up two volumes of this gas; ether can absorb two volumes; oil of turpentine two volumes and a half; and olive oil one volume by agitation at common temperatures and pressure; consequently, when a vessel of olefiant gas is transferred to a bath of any of these liquids and agitated, absorption quickly takes place.

Examined in this way, I have found no specimen of olefiant gas that is entirely absorbed; a residue always remains, which, though I have not yet had time to examine it accurately, appears to be light carburetted hydrogen; and I have no doubt that this is the substance which has mainly interfered in my former results. This substance appears to be produced in every stage of the preparation of olefiant gas. On taking six different portions of gas at different equal intervals, from first to last, during one process of preparation, after removing the sulphurous and carbonic acid and the ether as before described, then the following was the proportion per cent. of insoluble gas in the remainder when agitated with oil of turpentine, 10.5; 10; 10.1; 13.1; 28.3; 61.8. Whether carbonic oxide was present in any of these undissolved portions I cannot at present say.

In reference to the part dissolved, I wish as yet to guard myself from being supposed to assume that it is one uniform substance; there is indeed little doubt that the contrary is true; for whilst a volume of oil of turpentine introduced into twenty times its volume of olefiant

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\* Water, as BERZELIUS and others have pointed out, dissolves about  $\frac{1}{4}$ th its volume of olefiant gas, but I find that it also leaves an insoluble residue, which burns like light carburetted hydrogen.

gas cleared from ether and the acids, absorbs  $2\frac{1}{2}$  volumes of the gas, the same volume of fresh oil of turpentine brought into similar contact with abundance of the gas which remains when one-half has been removed by solution only dissolved 1.54 part, yet there was an abundant surplus of gas which would dissolve in fresh oil of turpentine at this latter rate. When two-thirds of a portion of fresh olefant gas were removed by solution, the most soluble portion of that which remained required its bulk of fresh oil of turpentine to dissolve it. Hence at first one volume of camphine dissolved 2.50, but when the richer portion of the gas was removed, one volume dissolved 1.54 part; and when still more of the gas was taken away by solution, one volume of camphine dissolved only one volume of the gas. This can only be accounted for by the presence of various compounds in the soluble portion of the gas.

A portion of good olefant gas was prepared, well-agitated with its bulk of water in close vessels, left over lime and water for three days, and then condensed as before. When much liquid was condensed, a considerable proportion was allowed to escape to sweep out the uncondensed atmosphere and the more condensable vapours; and then the following pressures were observed:—

FAHR. °	Atmospheres.	FAHR. °	Atmospheres.	FAHR. °	Atmospheres.
—105 .	4.60	—65 .	8.30	—30 .	16.22
—100 .	4.82	—60 .	9.14	—25 .	17.75
—95 .	5.10	—55 .	10.07	—20 .	19.38
—90 .	5.44	—50 .	11.10	—15 .	21.11
—85 .	5.84	—45 .	12.23	—10 .	22.94
—80 .	6.32	—40 .	13.46	—5 .	24.87
—75 .	6.89	—35 .	14.79	0 .	26.90
—70 .	7.55				

On examining the form of the curve given by these pressures, it is very evident that, as on former occasions,

the pressures at low temperatures are too great to allow the condensed liquid to be considered as one uniform body, and the form of the curve at the higher pressures is quite enough to prove that no ether was present either in this or the former fluids. On permitting the liquid in the tube to expand into gas, and treating 100 parts of that gas with oil of turpentine, eighty-nine parts were dissolved, and eleven parts remained insoluble. There can be no doubt that the presence of this latter substance, soluble as it is under pressure in the more condensable portions, is the cause of the irregularity of the curve, and the too high pressure at the lower temperatures.

The ethereal solution of olefiant gas being mixed with eight or nine times its volume of water, dissolved and gradually minute bubbles of gas appeared, the separation of which was hastened by a little heat. In this way about half the gas dissolved was re-obtained, and burnt like very rich olefiant gas. One volume of the alcoholic solution, with two volumes of water, gave very little appearance of separating gas. Even the application of heat did not at first cause the separation, but gradually about half the dissolved olefiant gas was liberated.

The separation of the dissolved gas by water, heat, or change of pressure from its solutions, will evidently supply means of procuring olefiant gas in a greater state of purity than heretofore; the power of forming these solutions will also very much assist in the correct analysis of mixtures of hydrocarbons. I find that light carburetted hydrogen is hardly sensibly soluble in alcohol or ether, and in oil of turpentine the proportion dissolved is not probably  $\frac{1}{10}$ th the volume of the fluid employed; but the further development of these points I must leave for the present.

*Carbonic acid.*—This liquid may be retained in glass tubes furnished with cemented caps, and closed by plugs

or stop-cocks, as described, but it is important to remember the softening action on the cement which, being continued, at last reduces its strength below the necessary point. A tube of this kind was arranged on the 10th of January and left; on the 15th of February it exploded, not by any fracture of the tube, for that remained unbroken, but simply by throwing off the cap through a failure of the cement. Hence the cement joints should not be used for long experiments, but only for those enduring for a few days.

*Oxygen.*—Chlorate of potassa was melted and pulverized. Oxide of manganese was pulverized, heated red-hot for half an hour, mixed whilst hot with the chlorate, and the mixture put into a long strong glass generating tube with a cap cemented on, and this tube then attached to another with a gauge for condensation. The heat of a spirit lamp carefully applied produced the evolution of oxygen without any appearance of water, and the tubes, both hot and cold, sustained the force generated. In this manner the pressure of oxygen within the apparatus was raised as high as 58.5 atmospheres, whilst the temperature at the condensing place was reduced as low as  $-140^{\circ}$  FAHR., but no condensation appeared. A little above this pressure the cement of two of the caps began to leak, and I could carry the observation no further with this apparatus.

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From the former scanty and imperfect expressions of the elasticity of the vapour of the condensed gases, DOVE was led to put forth a suggestion,\* whether it might not ultimately appear that the same addition of heat (expressed in degrees of the thermometer) caused the same

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\* POGGENDORFF's *Annalen*, xxiii. 290; or THOMSON on Heat and Electricity, p. 9.

additional increase of expansive force for all gases or vapours in contact with their liquids, provided the observation began with the same pressure in all. Thus to obtain the difference between forty-four and fifty atmospheres of pressure, either with steam or nitrous oxide, nearly the same number of degrees of heat were required; to obtain the difference between twenty and twenty-five atmospheres, either with steam or muriatic acid, the same number were required. Such a law would of course make the rate of increasing expansive force the same for all bodies, and the curve laid down for steam would apply to every other vapour. This, however, does not appear to be the case. That the force of the vapour increases in a geometrical ratio for equal increments of heat is true for all bodies, but the ratio is not the same for all. As far as observations upon the following substances, namely, water, sulphurous acid, cyanogen, ammonia, arseniuretted hydrogen, sulphuretted hydrogen, muriatic acid, carbonic acid, olefiant gas, &c., justify any conclusion respecting a general law, it would appear that the more volatile a body is, the more rapidly does the force of its vapour increase by further addition of heat, commencing at a given point of pressure for all; thus for an increase of pressure from two to six atmospheres, the following number of degrees require to be added for the different bodies named: water  $69^{\circ}$ , sulphurous acid  $63^{\circ}$ , cyanogen  $64^{\circ}.5$ , ammonia  $60^{\circ}$ , arseniuretted hydrogen  $54^{\circ}$ , sulphuretted hydrogen  $56^{\circ}.5$ , muriatic acid  $43^{\circ}$ , carbonic acid  $32^{\circ}.5$ , nitrous oxide  $30^{\circ}$ ; and though some of these numbers are not in the exact order, and in other cases, as of olefiant gas and nitrous oxide, the curves sometimes even cross each other, these circumstances are easily accounted for by the facts already stated of irregular composition and the inevitable errors of first results. There seems every reason therefore to expect

that the increasing elasticity is directly as the volatility of the substance, and that by further and more correct observation of the forces, a general law may be deduced, by the aid of which, and only a single observation of the force of any vapour in contact with its fluid, its elasticity at any other temperature may be obtained.

Whether the same law may be expected to continue when the bodies approach near to the CAGNIARD DE LA TOUR state is doubtful. That state comes on sooner in reference to the pressure required, according as the liquid is lighter and more expansible by heat and its vapour heavier, hence indeed the great reason for its facile assumption by ether. But though with ether, alcohol and water, that substance which is most volatile takes up this state with the lowest pressure, it does not follow that it should always be so; and in fact we know that ether takes up this state at a pressure between thirty-seven and thirty-eight atmospheres, whereas muriatic acid, nitrous oxide, carbonic acid and olefiant gas, which are far more volatile, sustain a higher pressure than this without assuming that peculiar state, and whilst their vapours and liquids are still considerably different from each other. Now whether the curve which expresses the elastic force of the vapour of a given fluid for increasing temperatures continues undisturbed after that fluid has passed the CAGNIARD DE LA TOUR point or not is not known, and therefore it cannot well be anticipated whether the coming on of that state sooner or later with particular bodies will influence them in relation to the more general law referred to above.

The law already suggested gives great encouragement to the continuance of those efforts which are directed to the condensation of oxygen, hydrogen and nitrogen, by the attainment and application of lower temperatures than those yet applied. If to reduce carbonic acid from

the pressure of two atmospheres to that of one, we require to abstract only about half the number of degrees that is necessary to produce the same effect with sulphurous acid, it is to be expected that a far less abstraction will suffice to produce the same effect with nitrogen or hydrogen, so that further diminution of temperature and improved apparatus for pressure, may very well be expected to give us these bodies in the liquid or solid state.

*Royal Institution,  
Feb. 19, 1845.*



## APPENDIX.

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### MR. NORTHMORE'S PAPERS ON THE COMPRESSION OF GASES.

(Referred to at p. 28.)

#### I.

*Experiments on the remarkable Effects which take place in the Gases, by Change in their Habitudes, or elective Attractions, when mechanically compressed. By THOMAS NORTHMORE, Esq. In a Letter from the Author.\**

To Mr. NICHOLSON.

*Devonshire Street, Portland Place*

SIR,

*Dec. 17, 1805.*

IT was my intention to have postponed troubling you with the following experiments upon the condensation of the gases, until I had brought them to a greater degree of perfection; but being informed that several of them have already, by means of which I am ignorant, and probably in a mutilated state, found their way to the press, any further delay seems improper. If then you deem the present communication worthy a place in your interesting Journal, it is entirely at your service.

It had long ago occurred to me, that the various affinities which take place among the gases under the common pressure of the atmosphere, would undergo considerable

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\* [From Nicholson's Journal, vol. 12 (1805), pp. 368-373.]

alteration by the influence of condensation ; and the success attending the *violent* method adopted by the French chemists, which violence did not appear to me requisite, afforded additional encouragement to my undertaking some experiments upon the subject.

I communicated this to the late chemical operator in the Royal Institution, a gentleman eminently conversant in the science, and with whom I was then engaged in a series of experiments : he not only approved of my design, but seemed to think it not improbable that an extensive field might thus be opened to future discoveries. Whether these opinions are justly founded, is now left for you, Sir, and the public to judge.

In entering upon a field entirely new, obstacles were of course to be expected : nor without reason ; for though I had applied to one of the most eminent philosophical instrument-makers in London, Mr. Cuthbertson, yet I began to fear, even at the outset, that his skill would be set at defiance. The first instruments which he made for the present purpose were, a brass condensing-pump, with a lateral spring for the admission of the gas by means of stop-cock and bladder ; two pear-shaped receivers, one of metal of the capacity of seven cubic inches, and another of glass of about three and a half : these were connected by a brass stop-cock, having a screw at each end. The metallic receiver was soon found to be of little or no utility, as well on account of its liability to be acted upon by the generated acids ; its being too capacious, and thus consuming too large a quantity of gas : as because, though the result of an experiment might thus be known, yet the changes which the subjects might undergo would necessarily escape observation. The glass receiver obviated all these difficulties, and one or two imperfect experiments were performed with it : but the stop-cock speedily failed in its effect. For the power of

the compressed gases was so great, partly from their elasticity, and partly (where affinities had operated) from their corrosive quality, as absolutely to wear a channel in the metal of which the plug was made, and thus to effect their escape. But not to trouble you any further with the obstacles that occurred, and which are mentioned only to prevent unnecessary expence to others, I have at last, by Mr. Cuthbertson's assistance, procured a connecting-tube, to which a spring-valve is adapted that has hitherto answered every purpose.

The instruments which I now use, are, 1st. An exhausting syringe; 2d. A condensing-pump, with two lateral springs for different gases; 3d. The connecting spring-valve; and lastly, glass receivers, which should have been of various sizes, but the one mentioned above having burst, that which I have principally used in the following experiments, is of about five cubic inches and a quarter in capacity, and made of glass well annealed and a quarter of an inch in thickness. Besides these instruments, I have occasionally applied Mr. Cuthbertson's double syphon-gage, by which the number of atmospheres condensed in the receiver, or rather the elastic power of the gases, may be measured; but this is rendered of less service, because a stop-cock must then be placed between the receiver and spring-valve, which frequently impairs the whole experiment; and also because, after a certain degree of condensation, and more particularly upon the admixture of the gases, new affinities usually take place, which tend to diminish the elasticity: the greatest number of atmospheres my gage has yet measured, is eighteen. These, Sir, with some bladders and stop-cocks, various iron screw-keys, and a wooden guard for the legs in case of bursting, constitute the principal part of the requisite apparatus.

I now proceed to the experiments, premising that the

first four were made with the imperfect apparatus, when the gas was continually making its escape through the stop-cock.

#### *Experiment I.*

Into the glass receiver, of three cubic inches and a half capacity, were compressed in the following order : Hydrogen, two (wine) pints ; oxygen, two pints ; nitrogen, two pints. The result was, water which bedewed the inside of the receiver ; white floating vapours (probably the gaseous oxide of nitrogen) ; and an acid which reddened litmus paper. Mr. Accum was present at this experiment, and from his opinion, as well as from succeeding experiments, I have reason to think that this acid is the nitric.

#### *Experiment II.*

As a difference of arrangement in the order of the gases tends considerably to vary the result, I repeated the former experiment (having first poured a little lime-water into the receiver) by injecting first the oxygen, about three pints, then equal quantities of hydrogen and nitrogen. Much of this gas escaped, owing to the imperfection of the instrument ; but upon the affusion of the nitrogen, the white vapours again appeared in the receiver ; water seemed likewise to be formed ; and some yellow particles were seen floating upon the lime-water. These particles probably arose from the resinous substance, used in fastening on the cap of the receiver, being dissolved by the nitrous gas formed during condensation.

I would just observe, that the magnet *seemed* to be affected during this experiment ; but as there is iron used in the machine, this may be otherwise accounted for.

#### *Experiment III.*

Two pints of carbonic acid, and two of hydrogen, were

subjected to condensation. The result was, a watery vapour, and a gas of rather offensive smell.

*Experiment IV.*

Trying to inflame phosphorus by the condensation of atmospheric air, the bottom of the machine (where it had been repaired) burst out with an explosion. This happened when I had immersed the apparatus in water to discover where the air escaped. The receiver was full of the fumes of the phosphorus, which was itself dispersed in the vessel of water. I afterwards repeated this experiment with the more perfect apparatus, but I could not inflame the phosphorus, and the fumes which arose at first soon disappeared. There was just enough acid (probably phosphoric) formed in the inside of the receiver to tinge litmus.

*Experiment V.*

Having now the spring-valve, and new receiver of five cubic inches and a half capacity, I poured in two scruples of solution of potash, and then injected two pints of hidrogen, two of nitrogen, and three of oxigen. This quantity was hardly sufficient for the capacity of the receiver, and the result was only a smell of the gaseous oxide of nitrogen, a few yellowish fumes, and scarce enough acidity to tinge the edge of the test paper: of course, I could not effect the formation of nitrate of potash.

*Experiment VI.*

I now determined to begin with the nitrogen, which always appeared to me to undergo the most important chemical changes, and therefore injected two pints of nitrogen, three of oxigen, and two of hidrogen. Upon the condensation of the nitrogen, it speedily assumed an orange-red colour, which upon the accession of the oxigen, gradually diminished, and at length disappeared,

though at first it seemed rather deeper. A moist vapour, coating the inside of the receiver, arose upon the compression of the hydrogen, which moisture was strongly acid to the taste, coloured litmus, and, when very much diluted with water, acted upon silver.

#### *Experiment VII.*

Nearly the same as the last, but with different arrangement. The nitrogen, three pints and a half, was first introduced; then the hydrogen,\* two pints; and next the oxygen, three and a half. The nitrogen formed the orange-red colour as before; the hydrogen produced white clouds at first (*quare ammonia?*) which afterwards disappeared, and the orange-red colour became lighter; but upon the affusion of the oxygen, the colour did not disappear as in the last experiment, but, if any thing, became darker. I then injected two pints more of hydrogen, but this had little or no effect upon the colour. Some vapour was generated, which was, as usual, strongly acid.

#### *Experiment VIII.*

Previous to the bursting of the small receiver, I had put in it a scruple of lime, and condensed upon it three pints of nitrogen. The result was, a little reddish colour at first, which soon vanished. Upon repeating this experiment in the large receiver, I could produce no colour at all. In my present state of knowledge I am unable to account for this circumstance; but as soon as I get my new receivers of a smaller capacity, I mean to repeat the experiment.

Besides the above, I have made various other experiments with different gases, but I think it right to repeat them with greater accuracy before I submit them to the

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\* [Oxygen in the original.]

eye of the public: if upon that repetition they appear to me to be attended with results of sufficient importance to occupy a place in your Journal, I will take the liberty of communicating them to you, and am, Sir,

Your most obedient servant,

THO. NORTHMORE.

*P. S.* I think it necessary to add, that during the course of the above-mentioned experiments, there was a great variation of temperature in the atmosphere, from the heat of 70 degrees of Fahrenheit to the cold of 33.

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II.

*Experiments on condensed Gases. By T. NORTHMORE.\**

To Mr. NICHOLSON.

SIR,

I NOW take the liberty of presenting you with a continuation of my experiments upon the condensation of the gases, but first beg leave to make one observation, viz. that the quantity of gas said to be injected in each experiment, cannot (particularly in the preceding article) always be depended upon; for its tendency to escape is so constant and powerful, as frequently to elude every effort of mine to prevent it, and if it can find no other exit, it will sometimes escape by the side of the piston of the forcing pump. In the preceding experiments I have endeavoured as much as possible to obviate this evil, but not always with the success that I could wish.

Repeating the eighth experiment mentioned in my former letter, (see Vol. XII. p. 372-3) viz. the conden-

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\* [From Nicholson's Journal, vol. 13 (1806), pp. 233-236.]

sation of nitrogen upon lime, in order to discover the cause of the loss of colour in the nitrogen, I perceived that this arose from its fixation, and a nitrate of lime was the result. This experiment, on account of the elasticity of nitrogen previous to its change of habitude, requires some caution ; for one of my best receivers, three-eighths of an inch thick, was shivered in pieces with a violent explosion, after I had set it aside to see the effect of time upon the compressed gas.

*Experiment 9.* Upwards of a pint of nitrogen was condensed, and upon this I pumped one pint of gaseous oxide of carbon. The colour of the nitrogen was destroyed ; nitrous acid was formed ; and upon collecting the liberated gaseous oxide, it burnt not unlike alcohol. The two gases together were at first highly elastic.

From the facility with which nitrogen becomes united and fixed in various bodies, and from its expansive force when liberated from that state, I know not whether I am sufficiently warranted in suggesting an opinion, that the explosive force of various compounds may in a great measure be attributed to the sudden liberation of this fixed gas. To this cause I partly attribute the fulminating silver of Berthollet ; the fulminating gold, and various nitrates ; and the detonation which accompanies the decomposition of ammoniac by oxygenated muriatic acid gas.

*Exp. 10.* Having been unsuccessful in my endeavours to inflame phosphorus by the compression of atmospheric air, (see *Exp. 4.*) I now tried oxygen, but with little better effect. The phosphorus appeared to be somewhat discoloured, and I thought had a tendency to liquify, as it does when put upon a heated plate of iron. Indeed I have no doubt that some heat is generated by the condensation of air, since the thermometer rises upon external application to the receiver.



*Exp. 11.* Upon the compression of nearly two pints of oxygenated muriatic acid gas in a receiver two and a quarter cubic inches capacity, it speedily became converted into a yellow *fluid*, of such extreme volatility under the common pressure of the atmosphere, that it instantly evaporates upon opening the screw of the receiver. I need not add, that this fluid, so highly concentrated, is of a most insupportable pungency. When atmospheric air was pumped into the empty receiver, it was speedily filled with dense white fumes. There was a trifling residue of a yellowish substance left after the evaporation, which probably arose from a small portion of the oil and grease used in the machine, mixed with some of the concentrated gas; it yielded to sulphuric ether, and destroyed vegetable colours.

This gas is very injurious to the machine, and on that account difficult to work.

*Exp. 12.* Upon half a pint of oxygen was injected one pint of oxygenated muriatic acid gas. The result was a thicker substance, which did not so soon evaporate, and a yellowish mass was left behind.

*Exp. 13.* Upon half a pint of nitrogen was injected one pint of oxy-muriatic gas. The result was a still thicker substance, and the yellow colour deeper, nor did it appear to act so powerfully upon vegetable colours. Much of the grease of the machine was carried down in both these last experiments, which formed part of the yellow residue, and yielded only to ether.

*Exp. 14.* Having condensed about a pint of carbonic acid, the receiver very unexpectedly burst with violence. This circumstance I attribute to the vicinity of the furnace, and I mention it to guard others against standing too near a fire in these experiments; nor perhaps may it be useless to add another precaution, that of using

goggles, or at least a thick plate of glass when examining the results.

I now took a new receiver of three cubic inches of capacity, and pumped in one pint of carbonic acid, and upon this rather more than a pint of oxygenated muriatic acid gas.

The union produced a light sap-green colour, but no fluid, though as usual the oil of the machine had retained enough efficacy to destroy vegetable colours.

*Exp. 15.* Upon rather more than a pint of hydrogen, which was highly elastic, were compressed two pints of the oxygenated muriatic gas. The result was a light yellow-green colour, and no fluid. Some smoke or vapour seemed to issue out of the receiver upon turning the screw, and the gas was highly destructive of colouring matter.

*Exp. 16.* I now proceeded to the muriatic acid gas, and upon the condensation of a small quantity of it, a beautiful green coloured substance adhered to the side of the receiver, which had all the qualities of muriatic acid; but upon a large quantity, four pints, being condensed, the result was a yellowish-green glutinous substance, which does not evaporate, but is instantly absorbed by a few drops of water; it is of a highly pungent quality, being the essence of muriatic acid. As this gas easily becomes fluid, there is little or no elasticity, so that any quantity may be condensed without danger. My method of collecting this, and other gases which are absorbable by water, is by means of an exhausted florence flask (and in some cases an empty bladder) connected by a stop-cock with the extremity of the retort.

An idea here occurs to me, that the facility of fixation which is the property of the compressed muriatic, oxy-muriatic, and some other gases, may be made of some utility to the arts, since by previously pouring in

a little water, or other fluid into the receiver, an acid may be obtained of almost any degree of concentration.

*Exp. 17.* Having collected about a pint and a half of sulphureous acid gas, I proceeded to condense it in the three cubic inch receiver, but after a very few pumps the forcing piston became immoveable, being completely choked by the operation of the gas. A sufficient quantity however had been compressed to form vapour, and a thick slimy fluid of a dark yellow colour began to trickle down the sides of the receiver, which immediately evaporated with the most suffocating odour upon the removal of the pressure. This experiment corroborates the affirmation of Monge and Clouet, mentioned in Accum's chemistry, vol. I. p. 319. viz, that "by extreme artificial cold, and a strong pressure exerted at the same time, they rendered sulphureous acid gas fluid. From the injury which this gas does to the machine, it will be very difficult to perform any experiments upon its elective attractions with the other gases.

I remain, Sir,

Your obedient humble Servant,

T. NORTHMORE.

*Devonshire Street, Portland Place,*

*Feb. 15, 1806.*

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